

EXHIBIT 1



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(54) **MULTI-PIECE SOLID GOLF BALL**

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(58) Field of Search **473/357, 356,**
473/359, 372, 374, 371, 373; 524/194,
908, 432, 526, 534

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,683,257 A * 7/1987 Kakiuchi et al. 473/372
4,929,678 A * 5/1990 Hamada et al. 525/193
4,955,613 A * 9/1990 Gendreau et al. 260/998.14
5,252,652 A * 10/1993 Egashira et al. 473/372

5,733,205 A * 3/1998 Higuchi et al. 473/373
6,045,460 A * 4/2000 Hayashi et al. 473/376
6,194,505 B1 * 2/2001 Sone et al. 473/371
6,315,679 B1 * 11/2001 Sano 473/357

FOREIGN PATENT DOCUMENTS

EP 0 920 886 A2 6/1999
GB 2 324 740 A 11/1998

OTHER PUBLICATIONS

M. R. Farrally, A. J. Cochran, "Science and Golf III", 1999,
Human Kinetics, pp. 410, 412, 413.*
British Search Report, Oct. 17, 2002.

* cited by examiner

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(57) **ABSTRACT**

In a multi-piece solid golf ball comprising a solid core, an inner cover layer and an outer cover layer, the solid core is molded from a rubber composition comprising a base rubber composed of (a) 20–100 wt % of a polybutadiene having a high cis-1,4 content, a minimal 1,2 vinyl content and a viscosity η of up to 600 mPa·s at 25° C as a 5 wt % toluene solution, and satisfying a certain relationship between Mooney viscosity and polydispersity index in combination with (b) 0–80 wt % of another diene rubber, (c) an unsaturated carboxylic acid, (d) an organosulfur compound, (e) an inorganic filler, and (f) an organic peroxide; and the outer cover layer has a lower Shore D hardness than the inner cover layer. This combination of features gives the ball a good, soft feel upon impact and an excellent spin performance that provides increased distance.

9 Claims, No Drawings

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MULTI-PIECE SOLID GOLF BALL

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a multi-piece solid golf ball which has been imparted with a good, soft feel upon impact and an excellent spin performance that makes it possible to achieve an increased distance.

2. Prior Art

Various improvements are being made in formulating the polybutadiene used as the base rubber in golf balls so as to confer the balls with outstanding rebound characteristics.

For example, JP-A 62-89750 describes rubber compositions for use as the base rubber in solid golf balls, which compositions are arrived at by blending a polybutadiene having a Mooney viscosity of 70 to 100 and synthesized using a nickel or cobalt catalyst with another polybutadiene having a Mooney viscosity of 30 to 90 and synthesized using a lanthanide catalyst or polybutadiene having a Mooney viscosity of 20 to 50 and synthesized using a nickel or cobalt catalyst.

However, further improvements in the materials are required in the above art to achieve golf balls endowed with a good, soft feel upon impact and an excellent spin performance that helps increase the distance the ball travels when played.

JP-A 2-268778 describes golf balls molded using a blend composed of a polybutadiene having a Mooney viscosity of less than 50 and synthesized using a Group VIII catalyst in combination with a polybutadiene having a Mooney viscosity of less than 50 and synthesized with a lanthanide catalyst. However, golf balls with a good, soft feel upon impact and an excellent spin performance that helps increase the distance traveled by the ball cannot be obtained in this way.

The existing art also teaches multi-piece solid golf balls in which an intermediate layer is molded of a low-Mooney viscosity polybutadiene (JP-A 11-70187), solid golf balls molded from rubber compositions comprising a polybutadiene having a Mooney viscosity of 50 to 69 and synthesized using a nickel or cobalt catalyst in combination with a polybutadiene having a Mooney viscosity of 20 to 90 and synthesized using a lanthanide catalyst (JP-A 11-319148), solid golf balls molded from compositions based on a rubber having a 1,2 vinyl content of at most 2.0% and a weight-average molecular weight to number-average molecular weight ratio M_w/M_n of not more than 3.5 (JP-A 11-164912), golf balls molded from rubber compositions containing a high Mooney viscosity polybutadiene (JP-A 63-275356), and golf balls molded from rubber compositions comprising polybutadiene having a high number-average molecular weight in admixture with polybutadiene having a low number-average molecular weight (JP-A 3-151985). However, none of these prior-art golf balls truly have a good, soft feel upon impact and an excellent spin performance that helps increase the distance traveled by the ball.

Golf balls having a cover composed of a relatively hard inner layer and a relatively soft outer layer have already been disclosed in JP-A 6-218078, JP-A 6-343718, JP-A 7-24085, JP-A 9-239068, JP-A 10-151226, JP-A 10-201880, JP-A 11-104273, JP-A 11-104271, and Japanese Patent Applications No. 2000-274807 and 2000-274843. However, further improvements in distance are desired for the golf balls described in all of these specifications.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide multi-piece solid golf balls which are endowed with a good,

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soft feel when hit with a golf club and an excellent spin performance that helps increase the distance traveled by the ball when played.

The inventor has discovered that golf balls having a solid core, an inner cover layer over the core, and an outer cover layer over the inner cover layer, wherein the solid core is made of a rubber composition formulated from a particular type of base rubber combined in specific proportions with certain other materials, and the outer cover layer is softer than the inner cover layer, exhibit a good synergy from optimization of the solid core materials and an appropriate distribution of hardness between the inner and outer cover layers. Multi-piece solid golf balls thus constituted have a good, soft feel when hit with a golf club and an excellent spin performance that enables the ball to travel further when played.

Accordingly, the invention provides a multi-piece solid golf ball having a solid core, an inner cover layer enclosing the core, and an outer cover layer enclosing the inner cover layer. The solid core is molded from a rubber composition comprising 100 parts by weight of a base rubber composed of (a) 20 to 100 wt % of a polybutadiene having a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 2%, having a viscosity η at 25° C. as a 5 wt % solution in toluene of up to 600 mPa·s, and satisfying the relationship: $10B + 5 \leq A \leq 10B + 60$, wherein A is the Mooney viscosity (ML_{1+4} (100° C.)) of the polybutadiene and B is the ratio M_w/M_n between the weight-average molecular weight M_w and the number-average molecular weight M_n of the polybutadiene, in combination with (b) 0 to 80 wt % of a diene rubber other than component (a). The rubber composition includes also (c) 10 to 60 parts by weight of an unsaturated carboxylic acid and/or a metal salt thereof, (d) 0.1 to 5 parts by weight of an organosulfur compound, (e) 5 to 80 parts by weight of an inorganic filler, and (f) 0.1 to 5 parts by weight of an organic peroxide. The outer cover layer has a lower Shore D hardness than the inner cover layer.

The polybutadiene (a) is typically synthesized using a rare-earth catalyst.

Preferably, the diene rubber (b) includes 30 to 100 wt % of a second polybutadiene which has a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 5%, has a Mooney viscosity (ML_{1+4} (100° C.)) of not more than 55, and satisfies the relationship $\eta \leq 20A - 550$, wherein A is the Mooney viscosity (ML_{1+4} (100° C.)) of the second polybutadiene and η is the viscosity, in mPa·s, of the second polybutadiene at 25° C. as a 5 wt % solution in toluene. The second polybutadiene in component (b) is typically synthesized using a Group VIII catalyst.

In the multi-piece solid golf ball of the invention, it is generally advantageous for the inner cover layer to have a Shore D hardness of 50 to 80 and the outer cover layer to have a Shore D hardness of 35 to 60.

DETAILED DESCRIPTION OF THE INVENTION

The golf ball of the invention includes a solid core made of a rubber composition in which the base rubber is at least partly polybutadiene. It is critical that the base rubber contain as component (a) a specific amount of a polybutadiene in which the cis-1,4 and 1,2 vinyl contents, the viscosity η at 25° C. as a 5 wt % solution in toluene, and the relationship between the Mooney viscosity and the polydispersity index M_w/M_n have each been optimized.

That is, the polybutadiene (a) has a cis-1,4 content of at least 60%, preferably at least 80%, more preferably at least

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90%, and most preferably at least 95%; and has a 1,2 vinyl content of at most 2%, preferably at most 1.7%, more preferably at most 1.5%, and most preferably at most 1.3%. Outside of the above ranges, the resilience declines.

The polybutadiene (a) must also have a viscosity η at 25° C. as a 5 wt % solution in toluene of not more than 600 mPa·s. "Viscosity η at 25° C. as a 5 wt % solution in toluene" refers herein to the value in mPa·s units obtained by dissolving 2.28 g of the polybutadiene to be measured in 50 ml of toluene and carrying out measurement with a specified viscometer at 25° C. using a standard solution for the viscometer (JIS Z8809).

The polybutadiene (a) has a viscosity η at 25° C. as a 5 wt % solution in toluene of not more than 600 mPa·s, preferably not more than 550 mPa·s, more preferably not more than 500 mPa·s, even more preferably not more than 450 mPa·s, and most preferably not more than 400 mPa·s. Too high a viscosity η lowers the workability of the rubber composition. It is recommended that the viscosity η be at least 50 mPa·s, preferably at least 100 mPa·s, more preferably at least 150 mPa·s, and most preferably at least 200 mPa·s. Too low a viscosity η may lower the resilience.

In addition, the polybutadiene (a) must satisfy the relationship:

$$10B+5 \leq A \leq 10B+60,$$

wherein A is the Mooney viscosity (ML_{1+4} (100° C.)) of the polybutadiene and B is the ratio Mw/Mn between the weight-average molecular weight Mw and the number-average molecular weight Mn of the polybutadiene. A is preferably at least 10B+7, more preferably at least 10B+8 and most preferably at least 10B+9, but preferably not more than 10B+55, more preferably not more than 10B+50, and most preferably not more than 10B+45. If A is too low, the resilience declines. On the other hand, if A is too high, the workability of the rubber composition worsens.

It is recommended that the polybutadiene (a) have a Mooney viscosity (ML_{1+4} (100° C.)) of at least 20, preferably at least 30, more preferably at least 40, and most preferably at least 50, but not more than 80, preferably not more than 70, more preferably not more than 65, and most preferably not more than 60.

The term "Mooney viscosity" used herein refers in each case to an industrial index of viscosity as measured with a Mooney viscometer, which is a type of rotary plastometer (see JIS K6300). This value is represented by the symbol ML_{1+4} (100° C.), wherein "M" stands for Mooney viscosity, "L" stands for large rotor (L-type), "1+4" stands for a pre-heating time of 1 minute and a rotor rotation time of 4 minutes, and "100° C." indicates that measurement was carried out at a temperature of 100° C.

It is desirable for the polybutadiene (a) to be synthesized using a rare-earth catalyst. A known rare-earth catalyst may be used for this purpose.

Examples of suitable catalysts include lanthanide series rare-earth compounds, organoaluminum compounds, alumoxane, halogen-bearing compounds, optionally in combination with Lewis bases.

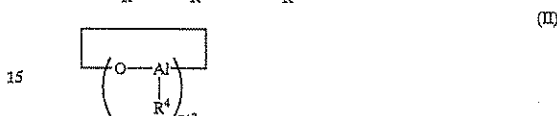
Examples of suitable lanthanide series rare-earth compounds include halides, carboxylates, alcoholates, thioalcoholates and amides of atomic number 57 to 71 metals.

Organoaluminum compounds that may be used include those of the formula $AlR^1R^2R^3$ (wherein R^1 , R^2 and R^3 are

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each independently a hydrogen or a hydrocarbon residue of 1 to 8 carbons).

Preferred alumoxanes include compounds of the structures shown in formulas (I) and (II) below. The alumoxane association complexes described in *Fine Chemical* 23, No. 9, 5 (1994), *J. Am. Chem. Soc.* 115, 4971 (1993), and *J. Am. Chem. Soc.* 117, 6465 (1995) are also acceptable.



In the above formulas, R^4 is a hydrocarbon group having 1 to 20 carbon atoms, and n is 2 or a larger integer.

Examples of halogen-bearing compounds that may be used include aluminum halides of the formula AlX_nR_{3-n} (wherein X is a halogen; R is a hydrocarbon residue of 1 to 20 carbons, such as an alkyl, aryl or aralkyl; and n is 1, 1.5, 2 or 3); strontium halides such as Me_2SrCl , Me_2SrCl_2 , $MeSrHCl_2$ and $MeSrCl_3$ (wherein "Me" stands for methyl); and other metal halides such as silicon tetrachloride, tin tetrachloride and titanium tetrachloride.

The Lewis base may be used to form a complex with the lanthanide series rare-earth compound. Illustrative examples include acetylacetone and ketone alcohols.

In the practice of the invention, the use of a neodymium catalyst composed in part of a neodymium compound as the lanthanide series rare-earth compound is advantageous because it enables a polybutadiene rubber having a high cis-1,4 content and a low 1,2 vinyl content to be obtained at an excellent polymerization activity. Preferred examples of such rare-earth catalysts include those mentioned in JP-A 11-35633.

The polymerization of butadiene in the presence of a rare-earth catalyst may be carried out by bulk polymerization or vapor phase polymerization, either with or without the use of solvent, and at a polymerization temperature in a range of generally -30° C. to +150° C., and preferably 10° C. to 100° C.

It is also possible for the polybutadiene (a) to be obtained by polymerization using the above-described rare-earth catalyst, followed by the reaction of an end group modifier with active end groups on the polymer.

Any known end group modifier may be used. Examples include compounds of types (1) to (6) described below:

- (1) halogenated organometallic compounds, halogenated metallic compounds and organometallic compounds of the general formulas $R^5_nM'X_{4-n}$, $M'X_4$, $M'X_3$, R^5_nM' ($-R^6-COOR^7$) $_{4-n}$ or $R^5_nM'(-R^6-COR^7)$ $_{4-n}$ (wherein R^5 and R^6 are each independently a hydrocarbon group of 1 to 20 carbons; R^7 is a hydrocarbon group of 1 to 20 carbons which may contain a carbonyl or ester moiety as a side chain; M' is a tin atom, silicon atom, germanium atom or phosphorus atom; X is a halogen atom; and n is an integer from 0 to 3);
- (2) heterocumulene compounds containing on the molecule a $Y=C=Z$ linkage (wherein Y is a carbon atom, oxygen atom, nitrogen atom or sulfur atom; and Z is an oxygen atom, nitrogen atom or sulfur atom);

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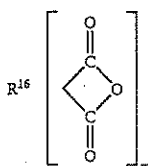
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- (3) three-membered heterocyclic compounds containing on the molecule the following bonds



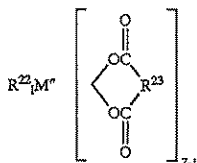
(wherein Y is an oxygen atom, a nitrogen atom or a sulfur atom);

- (4) halogenated isocyanate compounds;
 (5) carboxylic acids, acid halides, ester compounds, carbonate compounds or acid anhydrides of the formulas $R^8-(COOH)_m$, $R^9(COX)_m$, $R^{10}-(COO-R^{11})_m$, $R^{12}-OCOO-R^{13}$, $R^{14}-(COOCO-R^{15})_m$ or the following formula



(wherein R^8 to R^{16} are each independently a hydrocarbon group of 1 to 50 carbons; X is a halogen atom; and m is an integer from 1 to 5); and

- (6) carboxylic acid metal salts of the formula $R^{17}_1M^{18} (OCOR^{19})_{4-1}$, $R^{19}_1M^{18} (OCO-R^{20}-COOR^{21})_{4-1}$ or the following formula



(wherein R^{17} to R^{23} are each independently a hydrocarbon group of 1 to 20 carbons, M^{18} is a tin atom, a silicon atom or a germanium atom; and 1 is an integer from 0 to 3).

Illustrative examples of the end group modifiers of types (1) to (6) above and methods for their reaction are described in, for instance, JP-A 11-35633 and JP-A 7-268132.

In the practice of the invention, component (a) is included in the base rubber in an amount of at least 20 wt %, preferably at least 25 wt %, more preferably at least 30 wt %, and most preferably at least 35 wt %. The upper limit is 100 wt %, preferably not more than 90 wt %, more preferably not more than 80 wt %, and most preferably not more than 70 wt %.

In addition to component (a), the base rubber may include also a diene rubber (b) insofar as the objects of the invention are attainable. Specific examples of the diene rubbers (b) include polybutadiene rubber, styrene-butadiene rubber (SBR), natural rubber, polyisoprene rubber, and ethylene-propylene-diene rubber (EPDM). Any one or combination of two or more thereof may be used.

The diene rubber (b) is included together with component (a) in the base rubber in an amount of at least 0 wt %, preferably at least 10 wt %, more preferably at least 20 wt %, and most preferably at least 30 wt %, but not more than 80 wt %, preferably not more than 75 wt %, more preferably not more than 70 wt %, and most preferably not more than 65 wt %.

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In the practice of the invention, it is preferable for component (b) to include a polybutadiene rubber, and especially one for which the cis-1,4 and 1,2 vinyl contents, the Mooney viscosity, and the relationship between the Mooney viscosity and η have each been optimized. The polybutadiene serving as component (b) is referred to as "second polybutadiene" in order to distinguish it from the polybutadiene serving as component (a).

It is recommended that the second polybutadiene in component (b) have a cis-1,4 content of at least 60%, preferably at least 80%, more preferably at least 90%, and most preferably at least 95%, and that it have a 1,2 vinyl content of at most 5%, preferably at most 4.5%, more preferably at most 4.0%, and most preferably at most 3.5%.

It is recommended that the second polybutadiene have a Mooney viscosity of at least 10, preferably at least 20, more preferably at least 25, and most preferably at least 30, but not more than 55, preferably not more than 50, and most preferably not more than 45.

In the practice of the invention, it is recommended that the second polybutadiene be one that has been synthesized using a Group VIII catalyst. Exemplary Group VIII catalysts include nickel catalysts and cobalt catalysts.

Examples of suitable nickel catalysts include single-component systems such as nickel-kieselguhr, binary systems such as Raney nickel/titanium tetrachloride, and ternary systems such as nickel compound/organometallic compound/boron trifluoride etherate. Exemplary nickel compounds include reduced nickel on a carrier, Raney nickel, nickel oxide, nickel carboxylate and organonickel complexes. Exemplary organometallic compounds include trialkylaluminum compounds such as triethylaluminum, tri-n-propylaluminum, triisobutylaluminum and tri-n-hexylaluminum; alkylolithium compounds such as n-butyllithium, sec-butyllithium, tert-butyllithium and 1,4-dilithiobutane; and dialkylzinc compounds such as diethylzinc and dibutylzinc.

Examples of suitable cobalt catalysts include the following composed of cobalt or cobalt compounds: Raney cobalt, cobalt chloride, cobalt bromide, cobalt iodide, cobalt oxide, cobalt sulfate, cobalt carbonate, cobalt phosphate, cobalt phthalate, cobalt carbonyl, cobalt acetylacetonate, cobalt diethyldithiocarbamate, cobalt anilinium nitrite and cobalt dinitrosyl chloride. It is particularly advantageous to use the above in combination with a dialkylaluminum monochloride such as diethylaluminum monochloride or diisobutylaluminum monochloride; a trialkylaluminum such as triethylaluminum, tri-n-propylaluminum, triisobutylaluminum or tri-n-hexylaluminum; an alkyl aluminum sesquichloride such as ethylaluminum sesquichloride; or aluminum chloride.

Polymerization using the Group VIII catalysts described above, and especially a nickel or cobalt catalyst, can generally be carried out by a process in which the catalyst is continuously charged into the reactor together with the solvent and butadiene monomer, and the reaction conditions are suitably selected from a temperature range of 5 to 60° C. and a pressure range of atmospheric pressure to 70 plus atmospheres, so as to yield a product having the above-indicated Mooney viscosity.

It is also desirable for the second polybutadiene in component (b) to satisfy the relationship:

$$20A - 750 \leq \eta \leq 20A - 550$$

wherein η is the viscosity of the second polybutadiene at 25° C. as a 5 wt % solution in toluene and A is the Mooney viscosity (ML_{1+4} (100° C.)) of the second polybutadiene.

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The viscosity η is preferably at least 20A-700, more preferably at least 20A-680, and most preferably at least 20A-650, but preferably not more than 20A-560, more preferably not more than 20A-580, and most preferably not more than 20A-590. The use of a polybutadiene having such an optimized relationship of η and A, that suggests the high linearity of polybutadiene molecules, is effective for conferring better resilience and workability.

The second polybutadiene generally accounts for at least 30 wt %, preferably at least 50 wt %, and most preferably at least 70 wt %, and up to 100 wt %, preferably up to 90 wt %, and most preferably up to 80 wt %, of the diene rubber (b). By including the second polybutadiene within component (b) in the foregoing range, even better extrudability and hence, workability during manufacture can be conferred.

The solid core in the golf balls of the invention is molded from a rubber composition containing as essential components specific amounts of (c) an unsaturated carboxylic acid and/or metal salt thereof, (d) an organosulfur compound, (e) an inorganic filler and (f) an organic peroxide per 100 parts by weight of the base rubber.

Specific examples of unsaturated carboxylic acids that may be used as component (c) include acrylic acid, methacrylic acid, maleic acid and fumaric acid. Acrylic acid and methacrylic acid are especially preferred.

Specific examples of unsaturated carboxylic acid metal salts that may be used as component (c) include the zinc and magnesium salts of unsaturated fatty acids such as zinc methacrylate and zinc acrylate. Zinc acrylate is especially preferred.

The unsaturated carboxylic acid and/or metal salt thereof used as component (c) is included in an amount, per 100 parts by weight of the base rubber, of at least 10 parts by weight, preferably at least 15 parts by weight, and most preferably at least 20 parts by weight, but not more than 60 parts by weight, preferably not more than 50 parts by weight, more preferably not more than 45 parts by weight, and most preferably not more than 40 parts by weight. Too much component (c) results in excessive hardness, giving the golf ball a feel upon impact that is difficult for the player to endure. On the other hand, too little component (c) undesirably lowers the resilience.

The organosulfur compound (d) of the rubber composition is essential for imparting good resilience. Exemplary organosulfur compounds include thiophenol, thionaphthol, halogenated thiophenols, and metal salts thereof. Specific examples include pentachlorothiophenol, pentafluorothiophenol, pentabromothiophenol, p-chlorothiophenol, and zinc salts thereof, such as the zinc salt of pentachlorothiophenol; and organosulfur compounds having 2 to 4 sulfurs, such as diphenylpolysulfides, dibenzylpolysulfides, dibenzoylpolysulfides, dibenzothiazoylpolysulfides and dithiobenzoylpolysulfides. Diphenyl disulfide and the zinc salt of pentachlorothiophenol are especially preferred.

The organosulfur compound (d) is included in an amount, per 100 parts by weight of the base rubber, of at least 0.1 part by weight, preferably at least 0.2 part by weight, and most preferably at least 0.5 part by weight, but not more than 5 parts by weight, preferably not more than 4 parts by weight, more preferably not more than 3 parts by weight, and most preferably not more than 2 parts by weight. Too much organosulfur compound results in an excessively low hardness, whereas too little makes it impossible to enhance the resilience.

Examples of inorganic fillers that may be used as component (e) include zinc oxide, barium sulfate and calcium

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carbonate. The inorganic filler (e) is included in an amount, per 100 parts by weight of the base rubber, of at least 5 parts by weight, preferably at least 7 parts by weight, more preferably at least 10 parts by weight, and most preferably at least 13 parts by weight, but not more than 80 parts by weight, preferably not more than 50 parts by weight, more preferably not more than 45 parts by weight, and most preferably not more than 40 parts by weight. Too much or too little inorganic filler makes it impossible to achieve a golf ball core having an appropriate weight and good rebound characteristics.

The organic peroxide (f) may be a commercial product, suitable examples of which include Percumil D (manufactured by NOF Corporation), Perhexa 3M (manufactured by NOF Corporation) and Lupercol 231XL (manufactured by Atochem Co.). If necessary, two or more different organic peroxides may be mixed and used together.

The organic peroxide (f) is included in an amount, per 100 parts by weight of the base rubber, of at least 0.1 part by weight, preferably at least 0.3 part by weight, more preferably at least 0.5 part by weight, and most preferably at least 0.7 part by weight, but not more than 5 parts by weight, preferably not more than 4 parts by weight, more preferably not more than 3 parts by weight, and most preferably not more than 2 parts by weight. Too much or too little organic peroxide makes it impossible to achieve a ball having a good feel upon impact and good durability and rebound characteristics.

If necessary, the rubber composition may also include an antioxidant, suitable examples of which include such commercial products as Nocrac NS-6, Nocrac NS-30 (both made by Ouchi Shinko Chemical Industry Co., Ltd.), and Yoshinox 425 (made by Yoshitomi Pharmaceutical Industries, Ltd.). The use of such an antioxidant in an amount, per 100 parts by weight of the base rubber, of at least 0 part by weight, preferably at least 0.05 part by weight, more preferably at least 0.1 part by weight, and most preferably at least 0.2 part by weight, but not more than 3 parts by weight, preferably not more than 2 parts by weight, more preferably not more than 1 part by weight, and most preferably not more than 0.5 part by weight, is desirable for achieving good rebound characteristics and durability.

The solid core of the invention can be produced by vulcanizing and curing the above-described rubber composition using a method like that employed with known rubber compositions for golf balls. For example, vulcanization may be carried out at a temperature of 100 to 200° C. for a period of 10 to 40 minutes.

In the practice of the invention, the solid core has a hardness which is suitably adjusted according to its manner of use in the various golf ball constructions that may be employed and is not subject to any particular limitation. The core may have a cross-sectional hardness profile which is flat from the center to the surface thereof, or which varies from the center to the surface.

It is recommended that the solid core have a deflection, when subjected to a load of 980 N (100 kg), of at least 2.0 mm, preferably at least 2.5 mm, more preferably at least 2.8 mm, and most preferably at least 3.2 mm, but not more than 6.0 mm, preferably not more than 5.5 mm, more preferably not more than 5.0 mm, and most preferably not more than 4.5 mm. Too small a deformation may worsen the feel of the ball upon impact and, particularly on long shots such as with a driver in which the ball incurs a large deformation, may subject the ball to an excessive rise in spin, reducing the carry. On the other hand, if the solid core is too soft, the golf ball tends to have a dead feel when hit, an inadequate

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rebound that results in a poor carry, and a poor durability to cracking with repeated impact.

It is recommended that the solid core in the inventive golf ball have a diameter of at least 30.0 mm, preferably at least 32.0 mm, more preferably at least 34.0 mm, and most preferably at least 35.0 mm, but not more than 40.0 mm, preferably not more than 39.5 mm, and most preferably not more than 39.0 mm.

It is also recommended that the solid core have a specific gravity of at least 0.9, preferably at least 1.0, and most preferably at least 1.1, but not more than 1.4, preferably not more than 1.3, and most preferably not more than 1.2.

The golf ball of the invention is a multi-piece solid golf ball having a cover composed of at least two layers which are referred to herein as the "inner cover layer" and the "outer cover layer." Such cover layers can be produced from known cover stock. The cover stocks used to make both cover layers in the inventive golf ball may be composed primarily of a thermoplastic or thermoset polyurethane elastomer, polyester elastomer, ionomer resin, ionomer resin having a relatively high degree of neutralization, polyolefin elastomer or mixture thereof. Any one or mixture of two or more thereof may be used, although the use of a thermoplastic polyurethane elastomer, ionomer resin or ionomer resin having a relatively high degree of neutralization is especially preferred.

Illustrative examples of thermoplastic polyurethane elastomers that may be used for the above purpose include commercial products in which the diisocyanate is an aliphatic or aromatic compound, such as Pandex T7298, Pandex T7295, Pandex T7890, Pandex TR3080, Pandex T8290, Pandex T8295 and Pandex T1188 (all manufactured by DIC Bayer Polymer, Ltd.). Illustrative examples of suitable commercial ionomer resins include Surlyn 6320, Surlyn 8945, Surlyn 9945 and Surlyn 8120 (both products of E. I. du Pont de Nemours and Co., Inc.), and Himilan 1706, Himilan 1605, Himilan 1855, Himilan 1557, Himilan 1601 and Himilan AM7316 (all products of DuPont-Mitsui Polychemicals Co., Ltd.).

Together with the primary material described above, the cover stock may include also, as an optional material, polymers (e.g., thermoplastic elastomers) other than the foregoing. Specific examples of polymers that may be included as optional constituents include polyamide elastomers, styrene block elastomers, hydrogenated polybutadienes and ethylene-vinyl acetate (EVA) copolymers.

The multi-piece solid golf ball of the invention can be manufactured by any suitable known method without particular limitation. In one preferred method, the solid core is placed within a given injection mold, following which a predetermined method is used to successively inject over the core the above-described inner and outer cover layer materials. In another preferred method, each of the cover stocks is formed into a pair of half cups, and the resulting pairs are successively placed over the solid core and compression molded.

In the golf balls of the invention, it is critical that the outer cover layer have a lower Shore D hardness than the inner cover layer.

It is recommended that the inner cover layer have a Shore D hardness of at least 50, preferably at least 51, more preferably at least 52, and most preferably at least 53, but not more than 80, preferably not more than 75, more preferably not more than 70, and most preferably not more than 65.

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It is recommended that the outer cover layer have a Shore D hardness of at least 35, preferably at least 40, more preferably at least 45, and most preferably at least 48, but not more than 60, preferably not more than 58, more preferably not more than 56, and most preferably not more than 54.

As noted above, in the practice of the invention the outer cover layer must have a lower Shore D hardness than the inner cover layer. It is advantageous for the inner and outer cover layers to have a difference in Shore D hardness of at least 2, preferably at least 5, more preferably at least 7, and most preferably at least 9 Shore D hardness units, but not more than 30, preferably not more than 25, and most preferably not more than 20 Shore D hardness units.

It is recommended that the inner and outer cover layers have a respective thickness of at least 0.7 mm, and preferably at least 1.0 mm, but not more than 3.0 mm, preferably not more than 2.5 mm, even more preferably not more than 2.0 mm, and most preferably not more than 1.6 mm.

The multi-piece solid golf ball of the invention can be manufactured for competitive use by imparting the ball with a diameter and weight which conform with the Rules of Golf; that is, a diameter of at least 42.67 mm and a weight of not more than 45.93 g. It is recommended that the diameter be no more than 44.0 mm, preferably no more than 43.5 mm, and most preferably no more than 43.0 mm; and that the weight be at least 44.5 g, preferably at least 45.0 g, more preferably at least 45.1 g, and most preferably at least 45.2 g.

Multi-piece solid golf balls according to the present invention have a good, soft feel upon impact and an excellent spin performance that enable the ball to travel a greater distance when played.

EXAMPLES

The following examples and comparative examples are provided to illustrate the invention, and are not intended to limit the scope thereof.

Examples 1-5 & Comparative Examples 1-4

The core materials shown in Table 2 were formulated in the indicated amounts per 100 parts by weight of polybutadiene material composed of polybutadiene types (1) to (7) below in the proportions shown in Table 1. The resulting core formulations were blended in a kneader or on a roll mill, then molded under applied pressure at 150° C. for 20 minutes to form solid cores having a diameter of about 36.4 mm.

Types of Polybutadiene

- (1) BR01, made by JSR Corporation
- (2) BR11, made by JSR Corporation
- (3) UBE101, made by Ube Industries, Ltd.
- (4) HCBN-4, an experimental grade of polybutadiene made by JSR Corporation
- (5) HCBN-2, an experimental grade of polybutadiene made by JSR Corporation
- (6) Experimental grade #9100081 made by Firestone
- (7) Experimental grade #9100069 made by Firestone

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TABLE 1

Type	Catalyst	cis-1,4 content, %	1,2 vinyl content, %	Mooney viscosity (A)	Mw/Mn (B)	η	10B + 5	10B + 60	20A - 550
Polybutadiene									
(1)	Ni	96	2.5	44	4.2	150	47	102	330
(2)	Ni	96	2	44	4.4	270	49	104	330
(3)	Co	95	3	38	4.2	130	47	102	210
(4)	Nd	96	1.1	44	3.5	390	40	95	330
(5)	Nd	96	0.9	40	3.3	280	38	93	250
(6)	Nd	95	1.5	56	2.6	370	31	86	570
(7)	Nd	96	1.3	48	2.5	280	30	85	410

TABLE 2

	Example					Comparative Example			
	1	2	3	4	5	1	2	3	4
Rubber formulation (pbw)									
(1)						50			
(2)	70	30	50		50	50		50	
(3)				50			50		50
(4)	30								
(5)				50	50		50	50	50
(6)		70							
(7)			50						
Core formulation (pbw)									
Polybutadiene	100	100	100	100	100	100	100	100	100
Dicumyl peroxide	1.4	1.4	1.4	0.7	0.7	1.4	1.4	1.4	1.4
1,1-Bis(t-butylperoxy)-3,3,5-trimethylcyclohexane				0.3	0.3				
Zinc oxide	18	18	15.5	27	26	26	28.5	27	26
Antioxidant	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Zinc acrylate	27	27	31	30	32	32	28	30	32
Zinc salt of pentachlorothiophenol	1	1	2	1	1	1	0	1	1

The resulting solid cores were tested as described below to determine their deformation under 980 N (100 kg) loading and their rebound. The results are shown in Table 4.

Deformation Under 980 N Loading

Measured as the deflection (mm) of the solid core when subjected to a load of 980 N (100 kg).

Rebound

The initial velocity of the solid cores was measured with the same type of initial velocity instrument as used by the official regulating body—the United States Golf Association (USGA). Each rebound value shown in Table 4 is the difference between the initial velocity of the solid core obtained in that particular example and the initial velocity of the solid core obtained in Comparative Example 2.

In each example, the resulting solid core was placed in a given mold and the appropriate resin shown in Table 3 was injection-molded over the core, thereby producing an inner layer-covered core having a diameter of about 39.7 mm. The covered core was then transferred to a given mold, and the appropriate resin shown in Table 3 was injection molded over the covered core, yielding a three-piece solid golf ball having a diameter of about 42.7 mm and a weight of about 45.3 g. Trade names appearing in Table 3 are described below.

Himilan: An ionomer resin produced by DuPont-Mitsui Polychemicals Co., Ltd.

Surlyn: An ionomer resin produced by E. I. du Pont de Nemours and Co.

Dynaron: An E-EB-E block copolymer produced by JSR Corporation

Pandex: A polyurethane elastomer produced by Bayer-DIC Polymer, Ltd.

The properties of the resulting golf balls were determined as described below. The results are shown in Table 4.

Material Properties

The Shore D hardnesses of the inner cover layer and the outer cover layer were measured with a durometer by the test method described in ASTM D2240.

Golf Ball Properties

The carry and total distance were measured when the ball was hit at a head speed (HS) of 50 m/s with a driver (No. 1 Wood) mounted on a swing machine.

Feel

The feel of the ball when actually shot with a driver (No. 1 Wood) and putter was rated by five professional and five top-caliber amateur golfers as "Too hard," "Good" or "Too soft." The rating assigned most often to a particular ball was used as that ball's overall rating.

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TABLE 3

	A	B	C	D	E	F	G
Formulation (pbw)							
Himilan 1706	50	70					
Himilan 1605	50						
Himilan 1557							
Himilan 1855							
Himilan AM7316		12					
Surlyn 8945			35				
Surlyn 9945			35				
Surlyn 8120				100			
Dynaron 6100P			30				
Pandex T8290					50		
Pandex T8295					50	100	
Behenic acid		16					
Magnesium oxide		2					
Titanium dioxide	4	2	4	4	2.7	2.7	4

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Japanese patent application Ser. No. 2001-163238 is incorporated herein by reference.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in light of the above teachings. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without departing from the scope of the appended claims.

What is claimed is:

1. A multi-piece solid golf ball comprising a solid core, an inner cover layer and an outer cover layer, wherein the solid core is molded from a rubber composition comprising

100 parts by weight of a base rubber composed of (a) 20 to 100 wt % of a polybutadiene having a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 2%, having a viscosity η at 25° C. as a 5 wt % solution in toluene of up to 600 mPa·s, being synthesized using a rare-earth catalyst and satisfying the relationship: $10B+5 \leq A \leq 10B+60$, wherein A is the Mooney viscosity (ML_{1+4} (100° C.)) of the polybutadiene and B is the ratio Mw/Mn between the weight-average molecular weight Mw and the number-average molecular weight Mn of the polybutadiene, in combination with (b) 0 to 80 wt % of a diene rubber other than component (a),

TABLE 4

	Example					Comparative Example			
	1	2	3	4	5	1	2	3	4
<u>Core properties</u>									
Deflection (mm) under 980 N load	3.8	3.8	3.5	3.5	3.3	3.3	3.5	3.5	3.3
Specific gravity	1.15	1.15	1.15	1.21	1.21	1.21	1.21	1.21	1.21
Rebound (m/s)	+0.9	+0.9	+1.1	+0.7	+0.8	+0.3	0	+0.5	+0.5
<u>Inner cover layer</u>									
Type	A	B	C	A	B	B	A	D	D
Shore D hardness	63	60	56	63	60	60	63	45	45
Specific gravity	0.98	0.97	0.97	0.98	0.97	0.97	0.98	0.98	0.98
Thickness (mm)	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
<u>Outer cover layer</u>									
Type	E	F	F	G	G	G	G	G	A
Shore D hardness	47	51	51	53	53	53	53	53	63
Specific gravity	1.18	1.18	1.18	0.98	0.98	0.98	0.98	0.98	0.98
Thickness (mm)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
<u>Golf ball properties</u>									
When hit with No. 1 Wood at HS of 50 m/s									
Carry (m)	227.0	226.9	226.7	226.9	226.7	223.8	222.2	217.7	220.8
Total distance (m)	258.5	258.8	258.3	258.3	258.0	255.0	253.4	248.3	252.8
Spin rate (rpm)	3205	3153	3241	3125	3180	3182	3121	3305	3177
Feel on impact	good	good	good	good	good	good	good	too soft	good
Spin rate on approach shot (sand wedge; HS 20 m/s)	6323	6251	6226	6118	6111	6107	6113	6186	4308
Feel of ball	good	good	good	good	good	good	good	too soft	too hard

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(c) 10 to 60 parts by weight of an unsaturated carboxylic acid or a metal salt thereof or both,
 (d) 0.1 to 5 parts by weight of an organosulfur compound,
 (e) 5 to 80 parts by weight of an inorganic filler,
 (f) 0.1 to 5 parts by weight of an organic peroxide;
 the inner cover layer has a Shore D hardness of 50 to 80;
 the outer cover layer has a Shore D hardness of 35 to 60;
 and
 the outer cover layer has a lower Shore D hardness than the inner cover layer.
 2. The golf ball of claim 1, wherein the diene rubber (b) includes 30 to 100 wt % of a second polybutadiene which has a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 5%, has a Mooney viscosity (ML_{1+4} (100° C.)) of not more than 55, and satisfies the relationship:
 $\eta \leq 20A - 550$,
 wherein A is the Mooney viscosity (ML_{1+4} (100° C.)) of the second polybutadiene and η is the viscosity of the second polybutadiene, in mPa·s, at 25° C. as a 5 wt % solution in toluene.

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3. The golf ball of claim 1 wherein said polybutadiene (a) is synthesized by using neodymium catalyst.
 4. The golf ball of claim 1 wherein said polybutadiene (a) has a Mooney viscosity (ML_{1+4} (100° C.)) of 40 to 60.
 5. The golf ball of claim 1, wherein the outer cover layer and the inner cover layer have a difference in Shore D hardness of at least 5 units.
 6. The golf ball of claim 1, wherein the outer cover layer and the inner cover layer have a difference in Shore D hardness of at least 7 units.
 7. The golf ball of claim 1, wherein the outer cover layer and the inner cover layer have a difference in Shore D hardness of at least 9 units.
 8. The golf ball of claim 1, wherein said ball is three-piece construction consisting of a solid core, an inner cover layer and an outer cover layer.
 9. The golf ball of claim 2, wherein the second polybutadiene in component (b) is synthesized using a Group VIII catalyst.

* * * * *

EXHIBIT 2



US006612940B1

(12) **United States Patent**
Nesbitt et al.

(10) Patent No.: **US 6,612,940 B1**

(45) Date of Patent: ***Sep. 2, 2003**

(54) **GOLF BALL**

(75) Inventors: **R. Dennis Nesbitt**, Westfield, MA (US);
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John L. Nealon, Springfield, MA (US);
Michael J. Sullivan, Barrington, RI (US)

(73) Assignee: **Spalding Sports Worldwide, Inc.**,
Chicopee, MA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 141 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **09/710,809**

(22) Filed: **Nov. 9, 2000**

Related U.S. Application Data

(63) Continuation-in-part of application No. 09/371,994, filed on Aug. 11, 1999, now Pat. No. 6,315,684, which is a continuation-in-part of application No. 08/975,799, filed on Nov. 21, 1997, now Pat. No. 5,971,870, said application No. 09/490,181, filed on Jan. 22, 2002, is a continuation-in-part of application No. 09/226,727, filed on Jan. 7, 1999, now Pat. No. 6,394,915, and a continuation-in-part of application No. 09/226,340, filed on Jan. 6, 1999, now Pat. No. 6,277,920, each is a continuation-in-part of application No. 08/819,945, filed on Mar. 18, 1997, now Pat. No. 5,895,105, which is a continuation-in-part of application No. 08/370,224, filed on Jan. 9, 1995, now abandoned, which is a continuation of application No. 07/893,227, filed on Jun. 4, 1992, now abandoned, which is a continuation-in-part of application No. 07/874,066, filed on Apr. 24, 2002, now

abandoned
(60) Provisional application No. 60/116,846, filed on Jan. 22, 1999, provisional application No. 60/116,899, filed on Jan. 22, 1999, provisional application No. 60/116,900, filed on Jan. 22, 1999, and provisional application No. 60/117,328, filed on Jan. 22, 1999.

(51) Int. Cl.⁷ **A63B 37/06**

(52) U.S. Cl. **473/376**

(58) Field of Search **473/377, 351, 473/370, 371, 372, 376; 524/432**

(56) References Cited

U.S. PATENT DOCUMENTS

4,683,257 A * 7/1987 Kakiuchi et al. 524/432
4,955,613 A * 9/1990 Gendreau et al. 473/351
6,376,612 B1 * 4/2002 Nesbitt et al. 473/373

* cited by examiner

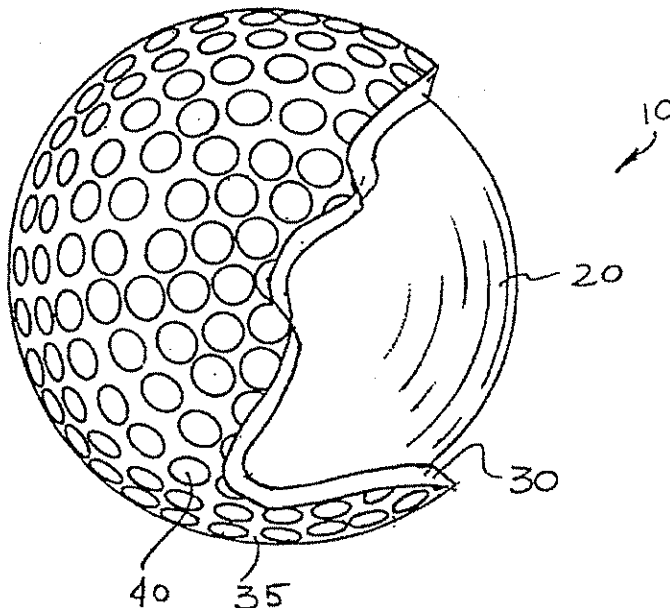
Primary Examiner—Mark S. Graham

Assistant Examiner—Raeann Gorden

(57) ABSTRACT

Disclosed herein is a golf ball utilizing a core that comprises at least two particular types of polybutadiene. In one aspect, a combination of a polybutadiene obtained from a cobalt catalyst is used in conjunction with a polybutadiene obtained from a neodymium catalyst. Also disclosed are golf balls comprising particular cover compositions. In one aspect, a cover composition is disclosed that includes a sodium ionomer, a magnesium ionomer, and a zinc ionomer. The golf balls exhibit improved distance while providing a soft sound and feel.

18 Claims, 15 Drawing Sheets



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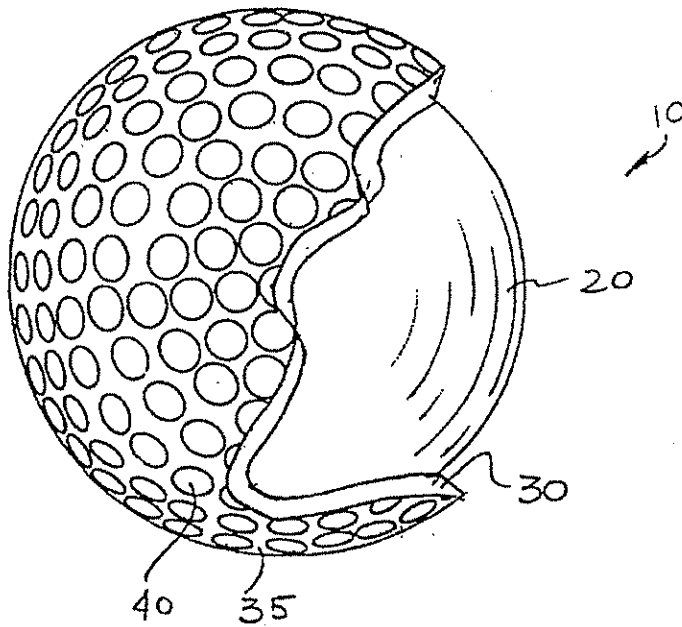


FIG. 1

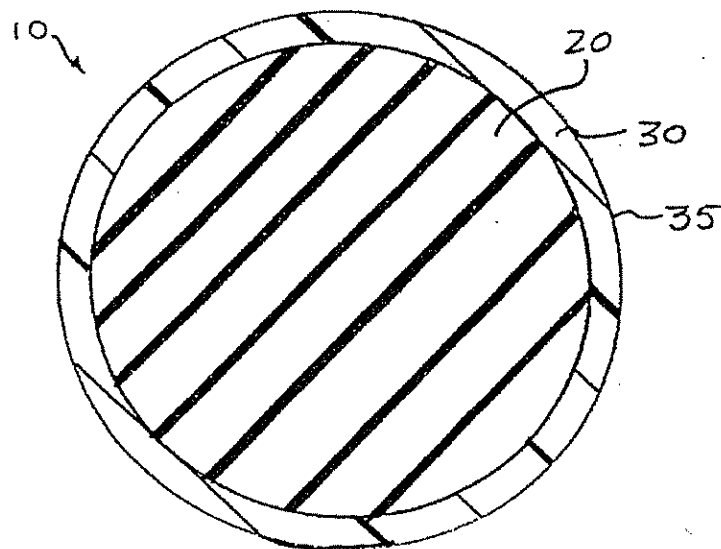


FIG. 2

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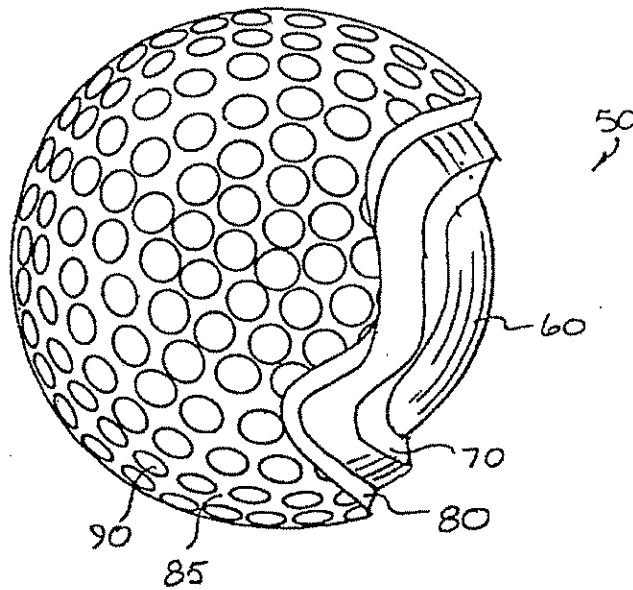


FIG. 3

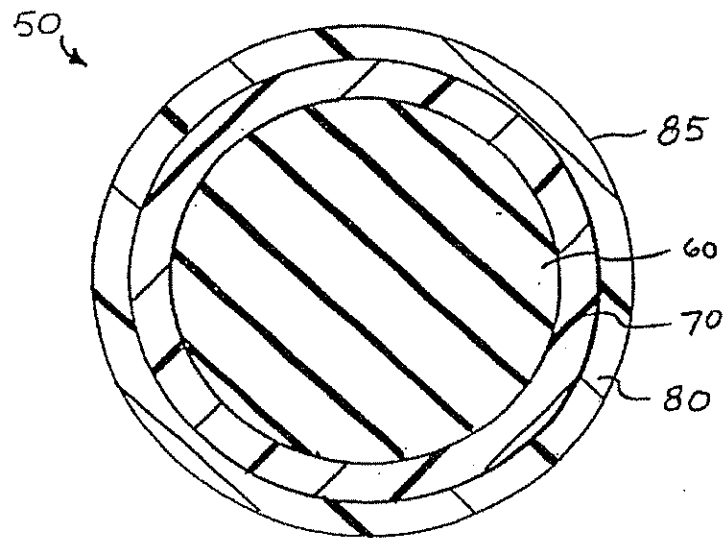


FIG. 4

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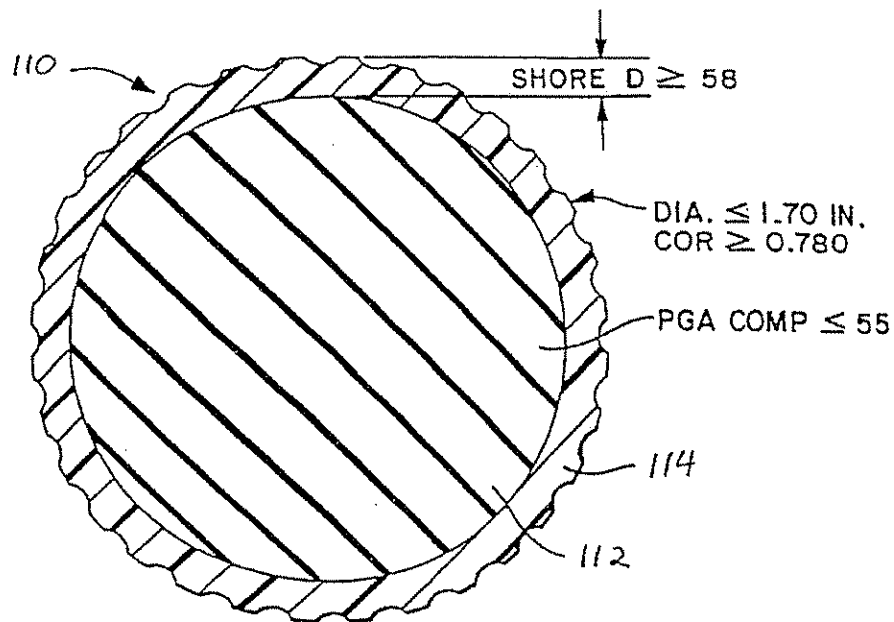


FIG. 5

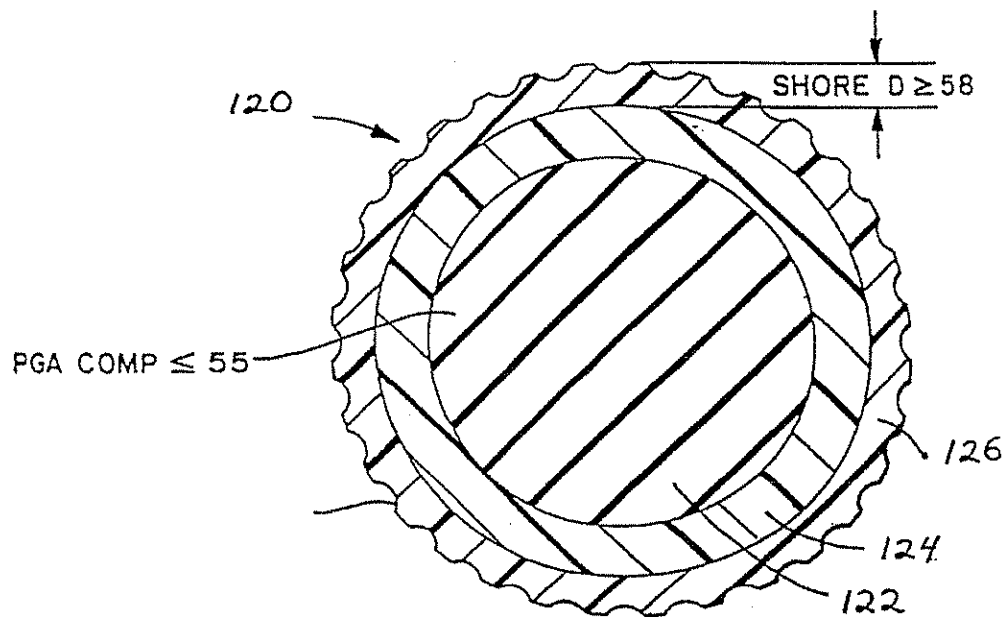


FIG. 6

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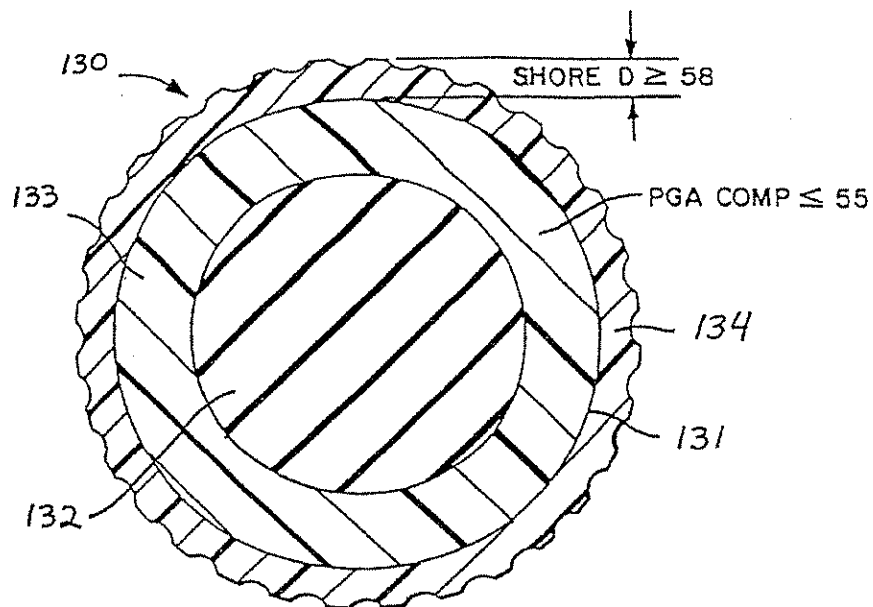


FIG. 7

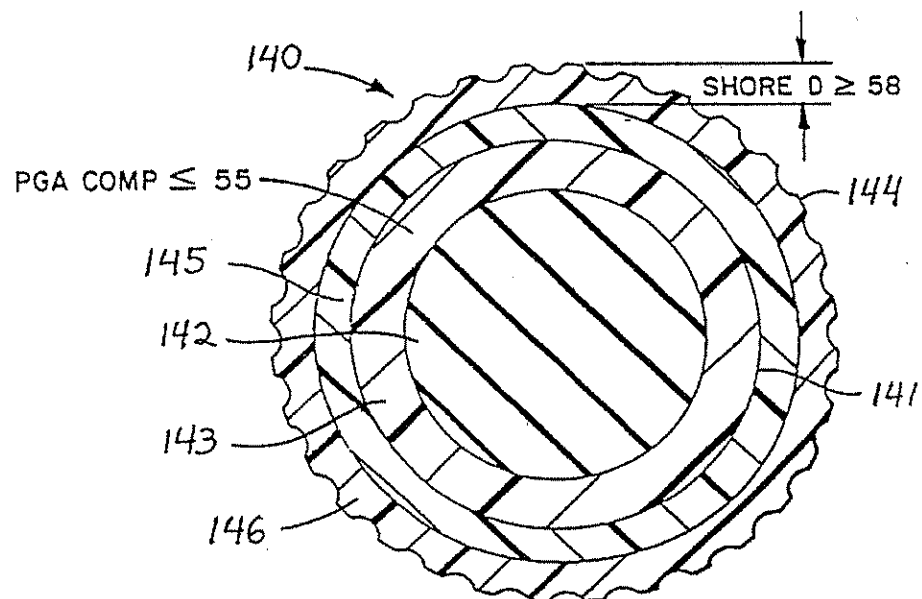


FIG. 8

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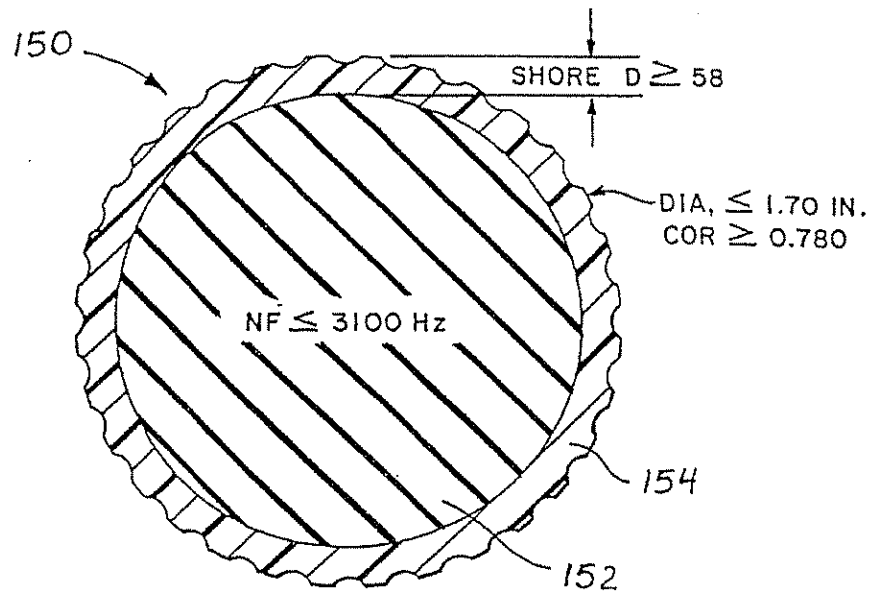


FIG. 9

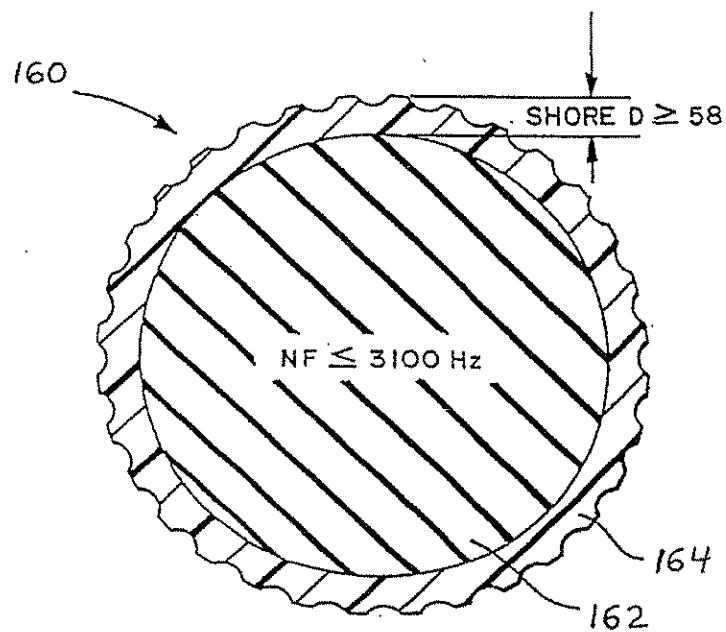


FIG. 10

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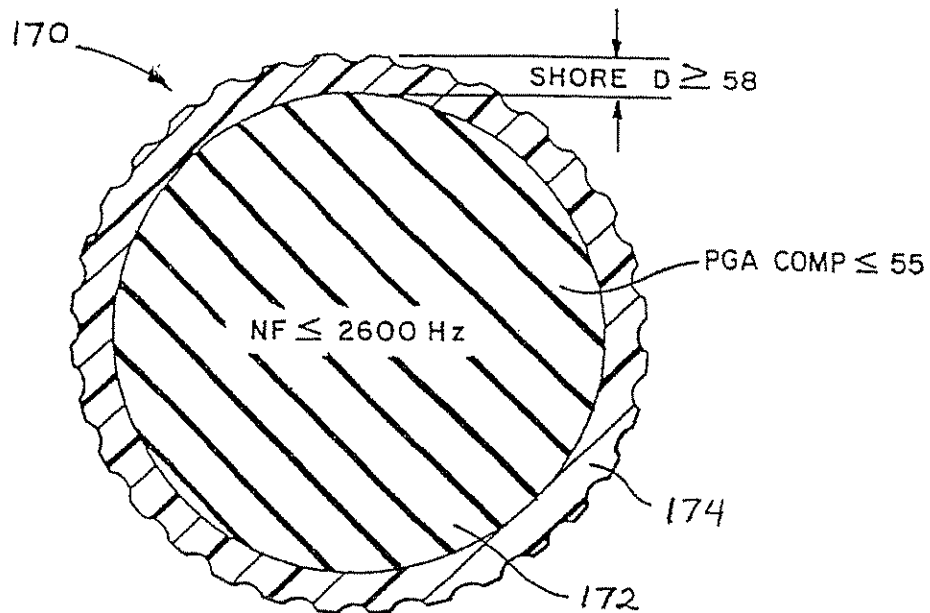


FIG. 11

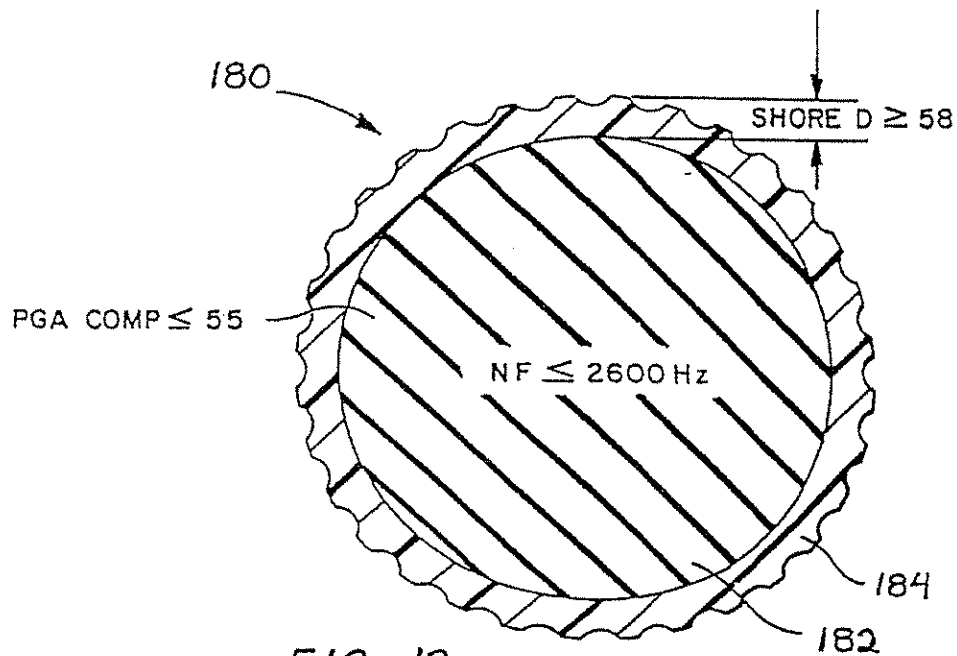


FIG. 12

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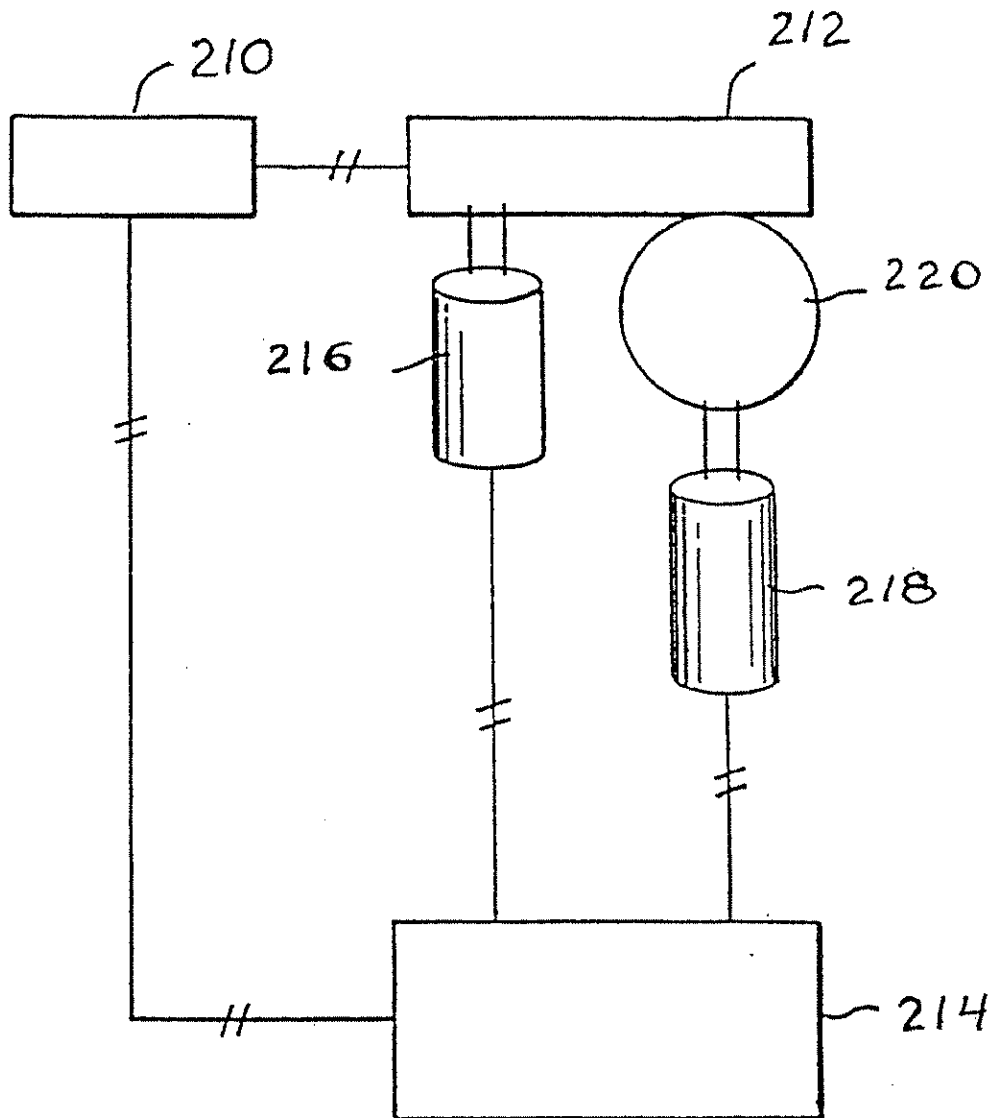


FIG. 13

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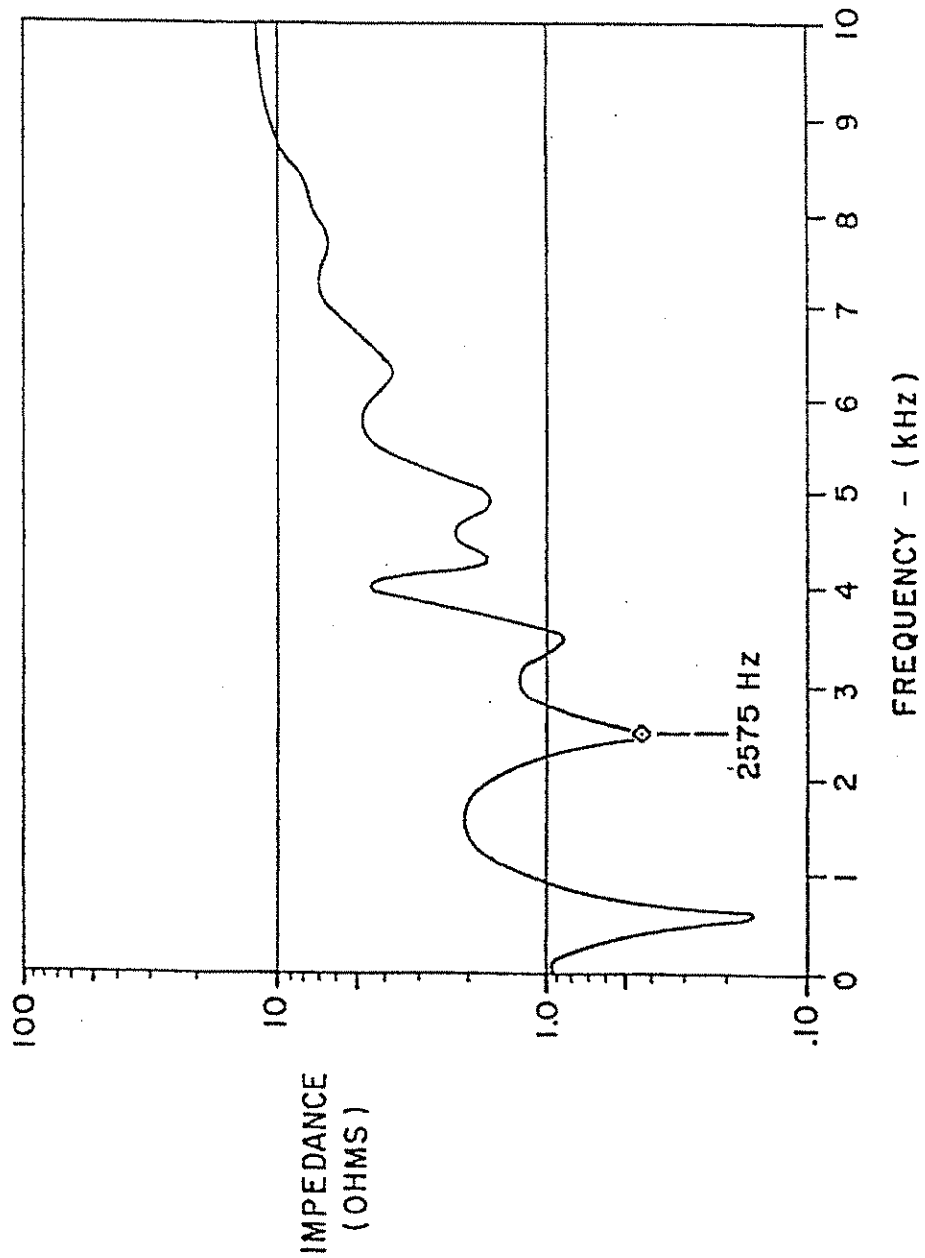


FIG. 14

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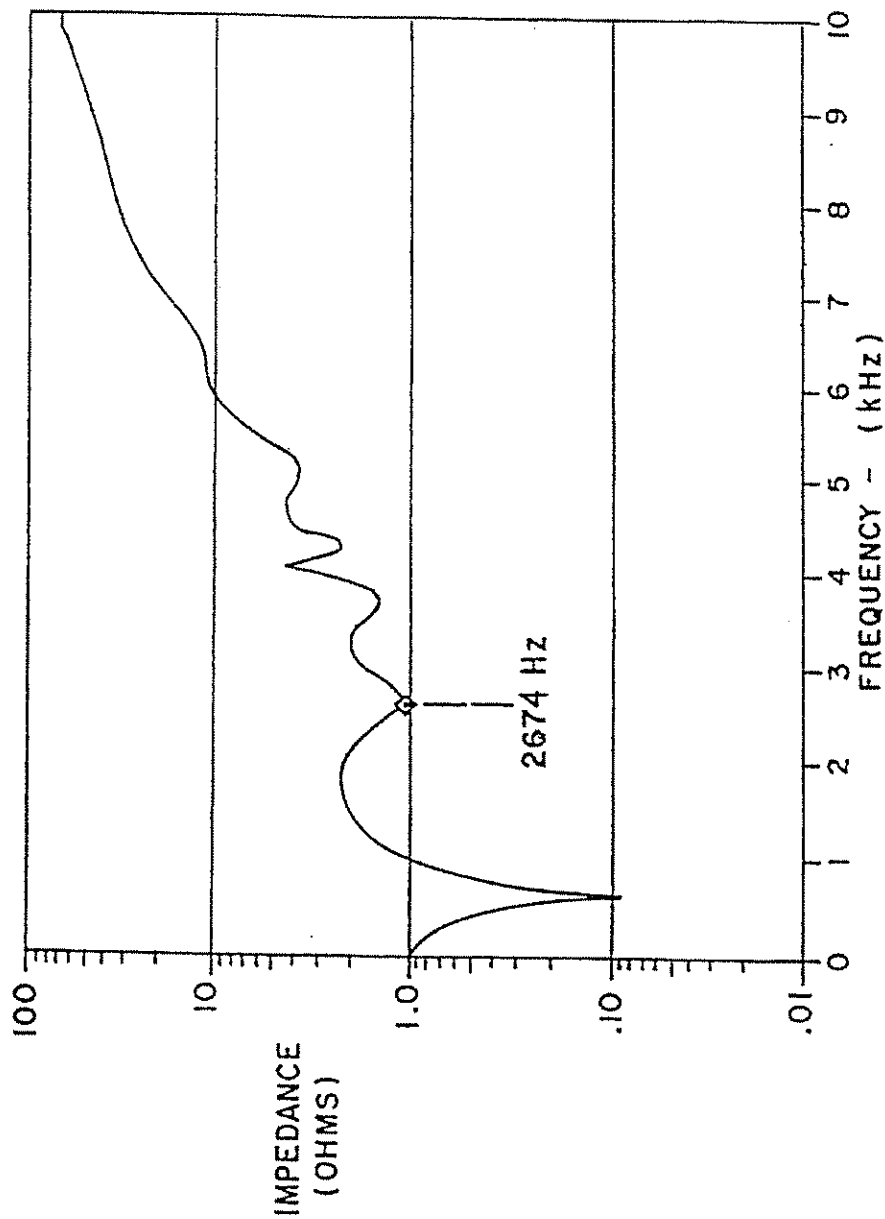


FIG. 15

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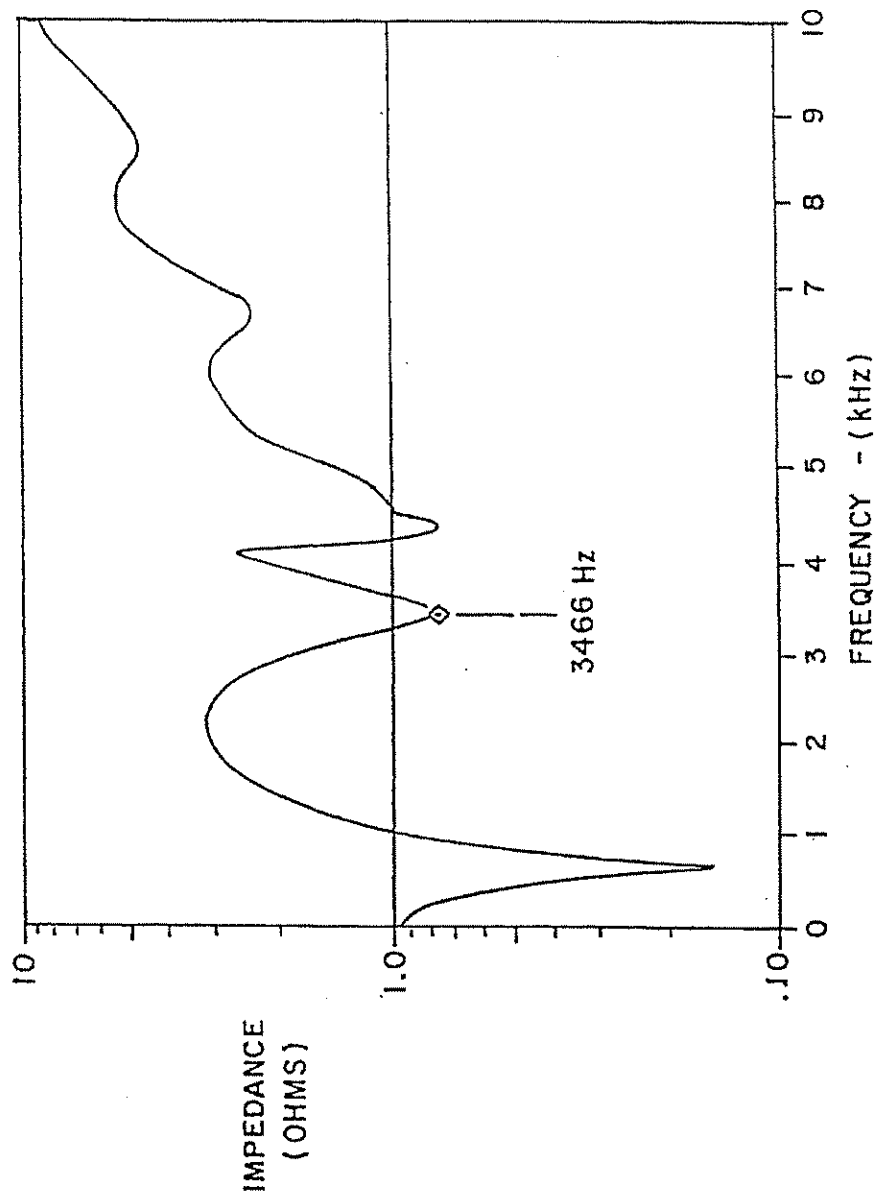


FIG. 16

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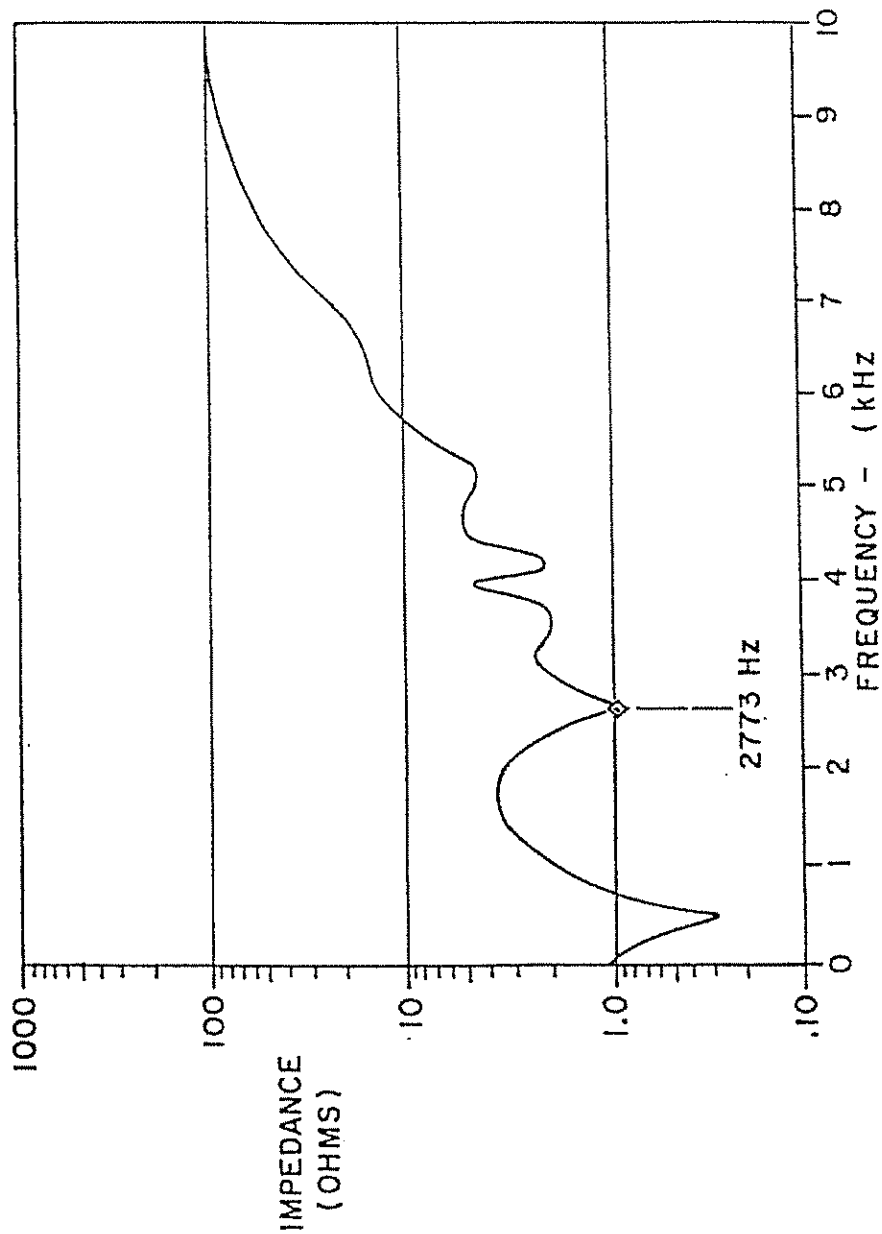


FIG. 17

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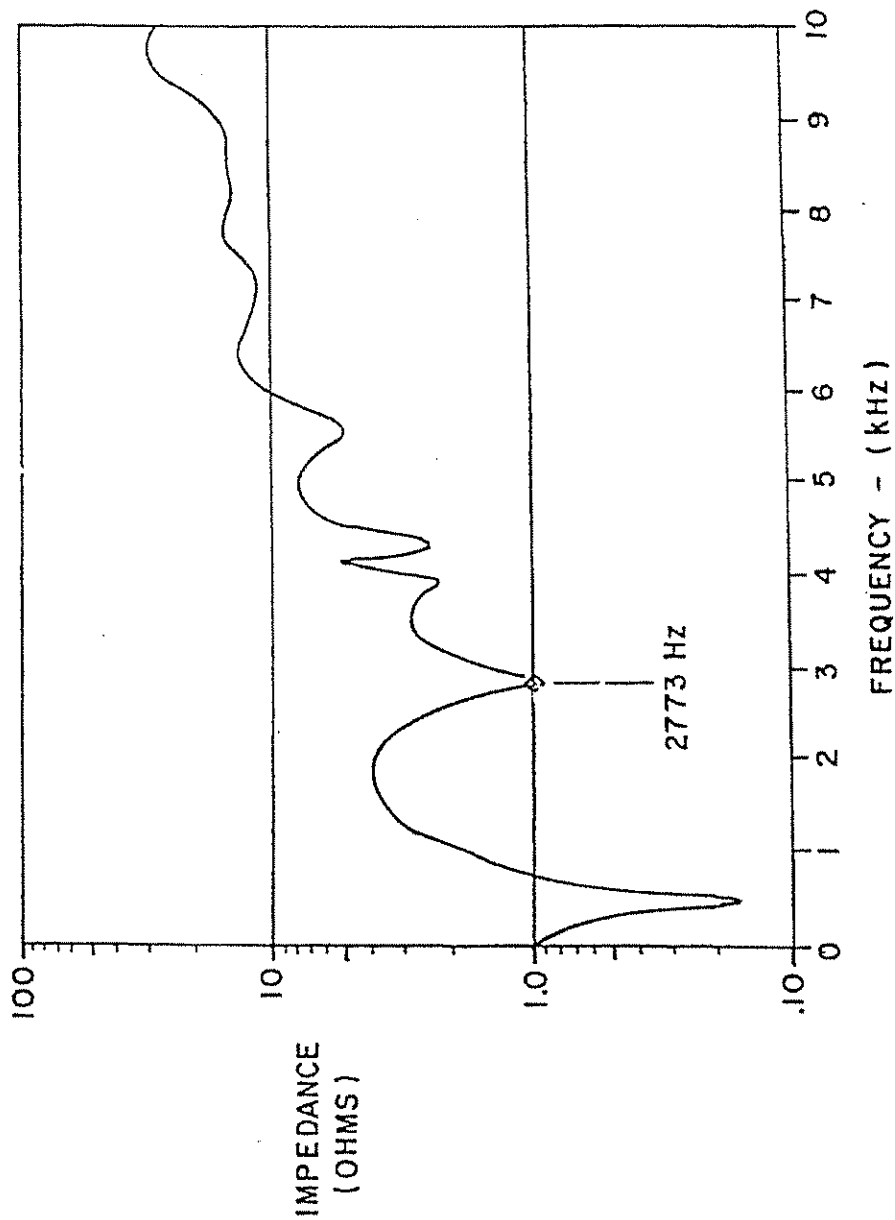


FIG. 18

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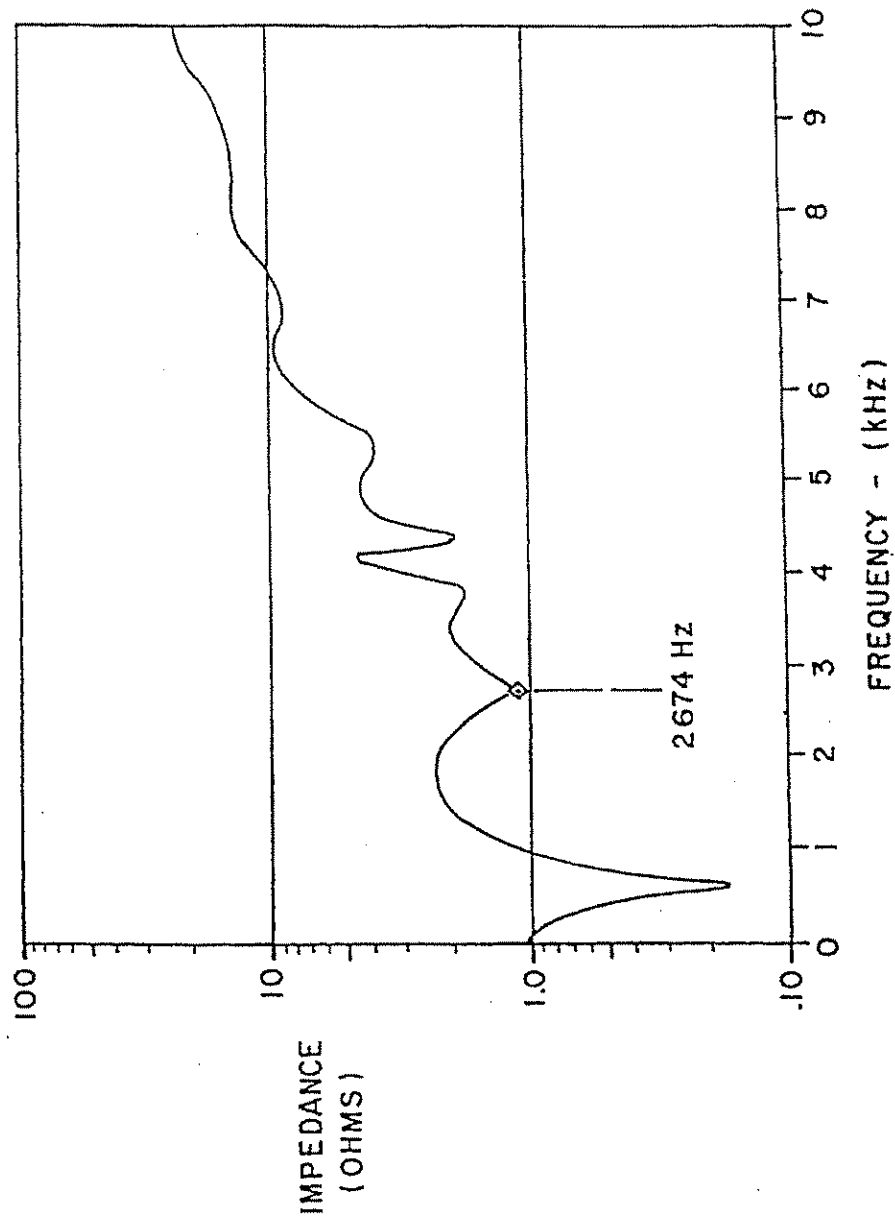


FIG. 19

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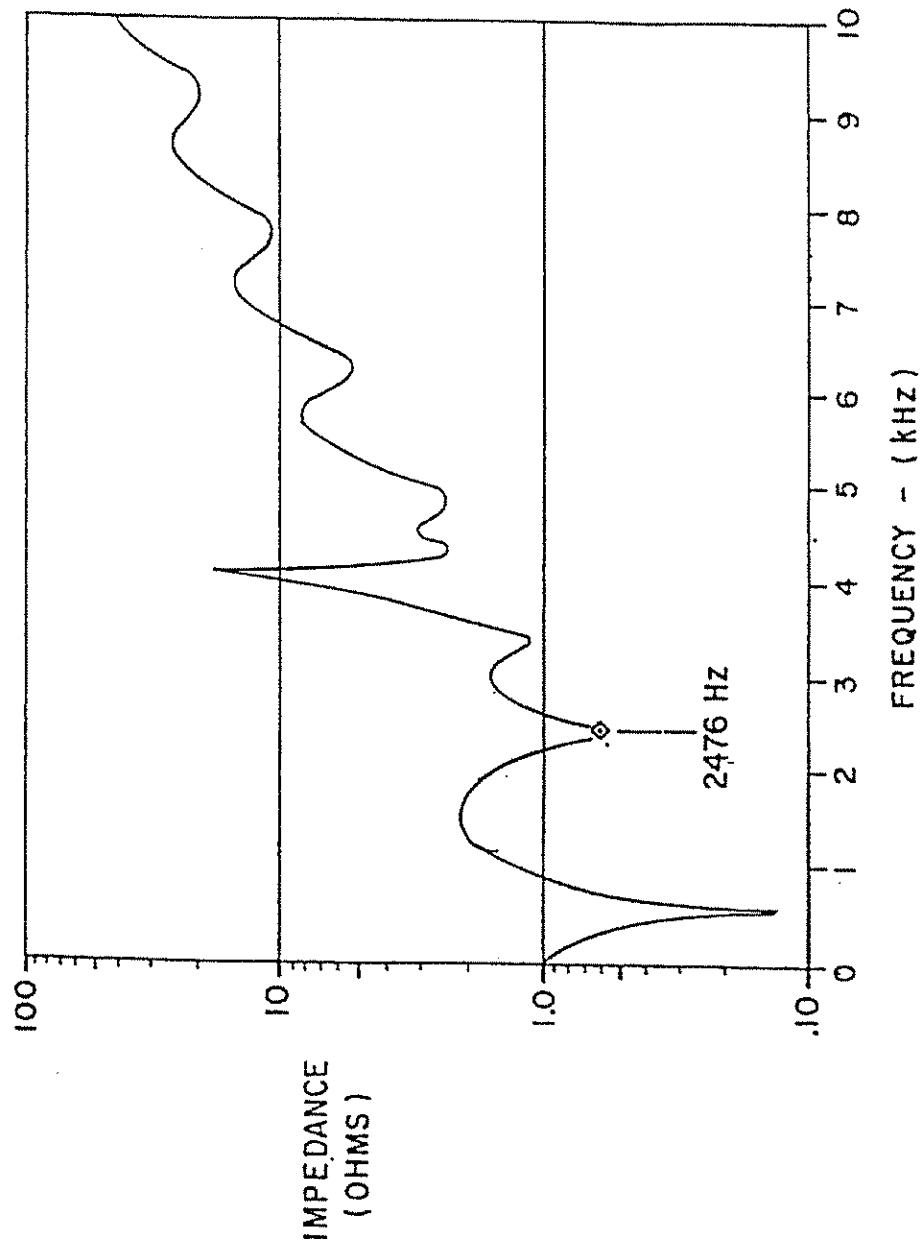


FIG. 20

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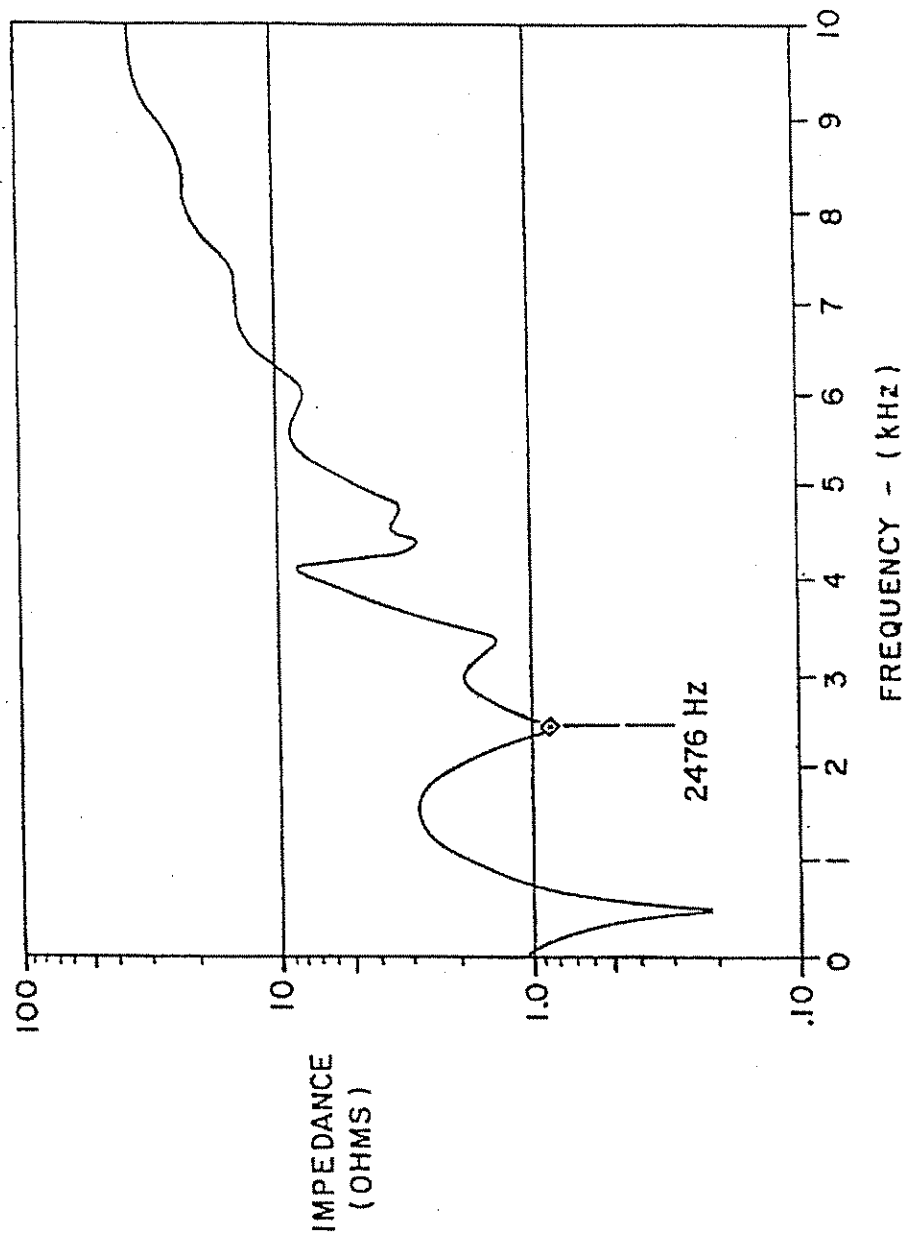


FIG. 21

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GOLF BALL

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of the filing date of U.S. Provisional Applications: 60/116,846, filed Jan. 22, 1999; 60/117,328, filed Jan. 22, 1999; 60/116,900, filed Jan. 22, 1999; 60/116,901, filed Jan. 22, 1999; 60/116,899, filed Jan. 22, 1999; and 60/116,870, filed Jan. 22, 1999. In addition, this application is a continuation of U.S. application Ser. No. 09/490,181, filed Jan. 22, 2002, now U.S. Pat. No. 6,422,953, which is a continuation-in-part application of U.S. application Ser. No. 09/371,994, filed Aug. 11, 1999, now U.S. Pat. No. 6,315,684, which is a continuation-in-part of U.S. application Ser. No. 08/975,799 filed Nov. 21, 1997, now U.S. Pat. No. 5,971,870. Application Ser. No. 09/490,181 is also a which continuation-in-part of U.S. application Ser. No. 09/226,727, filed on Jan. 7, 1999, now U.S. Pat. No. 6,394,915, and of U.S. application Ser. No. 09/226,340, filed on Jan. 6, 1999, now U.S. Pat. No. 6,277,920, both of which are continuations-in-part of application Ser. No. 08/819,945, filed on Mar. 18, 1997, now U.S. Pat. No. 5,895,105; which is a continuation of U.S. application Ser. No. 08/370,224 filed Jan. 9, 1995, now abandoned; which is a continuation of U.S. application Ser. No. 07/893,277 filed Jun. 4, 1992, now abandoned; and which is a continuation-in-part of U.S. application Ser. No. 07/874,066 filed Apr. 24, 1992, now abandoned.

FIELD OF THE INVENTION

The present invention is directed to golf balls utilizing improved polybutadiene compositions for use in molded golf ball cores in conjunction with a particular type of cover composition. In one aspect, the improved polybutadiene compositions utilize one or more particular butadiene rubbers synthesized through the use of neodymium and cobalt-containing catalysts. The polybutadiene is preferably an ultra-high Mooney viscosity polybutadiene. In another aspect, the improved polybutadiene compositions utilize a particular solid butadiene rubber that exhibits an ultra-high Mooney viscosity and/or a high molecular weight and a low dispersity. The use of such butadiene rubber and/or blend of butadiene rubbers increases the resiliency of the ball. In addition, significantly improved mixing properties are achieved. In another aspect, the golf balls feature particular cover constructions that result in the balls exhibiting a soft feel and particular mechanical impedance.

BACKGROUND OF THE INVENTION

Two of the principal properties involved in the performance of golf balls are resiliency and hardness. Resiliency is determined by the coefficient of restitution (referred to as "C.O.R."), also expressed as the constant "e", which is the ratio of the relative velocity of two elastic spheres after direct impact to that before impact, or more generally, the ratio of the outgoing velocity to incoming velocity of a rebounding ball. As a result, the coefficient of restitution (i.e. "e") can vary from zero to one, with one being equivalent to an elastic collision and zero being equivalent to an inelastic collision. Hardness is determined as the deformation (i.e. compression) of the ball under various load conditions applied across the ball's diameter. The lower the compression value, the harder the material.

Resiliency (C.O.R.), along with additional factors such as clubhead speed, angle of trajectory, and ball configuration (i.e. dimple pattern), generally determine the distance a ball

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will travel when hit. Since clubhead speed and the angle of trajectory are not factors easily controllable, particularly by golf ball manufacturers, the factors of concern among manufacturers are the coefficient of restitution (C.O.R.) and the surface configuration of the ball.

In this regard, the coefficient of restitution of a golf ball is generally measured by propelling a ball at a given speed against a hard surface and electronically measuring the ball's incoming and outgoing velocity. The coefficient of restitution must be carefully controlled in all commercial golf balls in order for the ball to be within the specifications regulated by the United States Golfers Association ("U.S.G.A."). Along this line, the U.S.G.A. standards indicate that a "regulation" ball cannot have an initial velocity (i.e. the speed off the club) exceeding 255 feet per second (250 feet per second with a 2% tolerance). Since the coefficient of restitution of a ball is related to the ball's initial velocity (i.e. as the C.O.R. of a ball is increased, the ball's initial velocity will also increase), it is highly desirable to produce a ball having a sufficiently high coefficient of restitution to closely approach the U.S.G.A. limit on initial velocity, while having an ample degree of hardness (i.e. impact resistance) to produce enhanced durability.

The coefficient of restitution (C.O.R.) in solid core balls is a function of the composition of the molded core and of the cover. In balls containing a wound core (i.e. balls comprising a liquid or solid center, elastic windings, and a cover), the coefficient of restitution is a function of not only the composition of the center and cover, but also the composition and tension of the elastomeric windings.

Polybutadiene has been utilized in forming golf ball cores. Prior artisans have investigated utilizing various grades of polybutadiene in core compositions. For example, such attempts are described in U.S. Pat. Nos. 5,385,440; 4,931,376; 4,683,257; 4,955,613; and 4,984,803; and in Japanese Patent References JP 58225138 and JP 7268132, all of which are hereby incorporated by reference. Although some of the core compositions described in these disclosures are satisfactory, a need remains for an improved composition for forming golf ball cores.

For example, U.S. Pat. No. 4,929,678 relates to a golf ball formed from a polybutadiene core composition having a broad Mooney viscosity of 45-90, preferably 50-70, and more preferably 55 to 65. However the dispersity of the core composition is limited to the range of 4.0 to 8.0, and preferably 4.0 to 6.0. According to the '678 patent, a dispersity of less than 4.0 produces deleterious workability.

Similarly, U.S. Pat. No. 5,082,285 generally discloses the preparation of a solid golf ball from an ultra-high molecular weight polybutadiene having a number average molecular weight of 40×10^4 or more, which has dispersity characteristics as noted. See also U.S. Pat. Nos. 4,974,852 and 5,585,440, wherein Mooney viscosity is discussed without reference to dispersity.

Accordingly, it is an object of the present invention to provide an improved polybutadiene composition which, when utilized to formulate golf ball cores, produces golf balls exhibiting enhanced C.O.R. without increasing hardness. An additional object of the invention is to produce a golf ball core from a polybutadiene composition having a high Mooney viscosity and/or a high molecular weight and low dispersity.

Accordingly, it is another object of the present invention to provide an improved core composition which, when utilized to formulate golf ball cores, produces golf balls exhibiting enhanced C.O.R. and improved processing.

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The spin rate and "feel" of a golf ball are particularly important aspects to consider when selecting a golf ball for play. A golf ball with the capacity to obtain a high rate of spin allows a skilled golfer the opportunity to maximize control over the ball. This is particularly beneficial when hitting a shot on an approach to the green.

Golfers have traditionally judged the softness of a ball by the sound of the ball as it is hit with a club. Soft golf balls tend to have a low frequency sound when struck with a club. This sound is associated with a soft feel and thus is desirable to a skilled golfer.

Balata covered wound golf balls are known for their soft feel and high spin rate potential. However, balata covered balls suffer from the drawback of low durability. Even in normal use, the balata covering can become cut and scuffed, making the ball unsuitable for further play. Furthermore, the coefficient of restitution of wound balls is reduced by low temperatures.

The problems associated with balata covered balls have resulted in the widespread use of durable ionomeric resins as golf ball covers. However, balls made with ionomer resin covers typically have PGA compression ratings in the range of 90-100. Those familiar with golf ball technology and manufacture will recognize that golf balls with PGA compression ratings in this range are considered to be somewhat harder than conventional balata covered balls. It would be useful to develop a golf ball having a durable cover which has the sound and feel of a balata covered wound ball.

These and other objects and features of the invention will be apparent from the following summary and description of the invention and from the claims.

SUMMARY OF THE INVENTION

The present invention achieves all of the foregoing objectives and provides, in a first aspect, a golf ball comprising a core that includes a particular combination of polybutadiene rubbers, and a cover disposed about the core which includes a specific combination of ionomer resins. The polybutadiene rubbers used in the particular combination include a first polybutadiene rubber that is obtained utilizing a cobalt catalyst and which exhibits a Mooney viscosity in the range of from about 70 to about 83. The combination of polybutadiene rubbers also includes a second polybutadiene rubber that is obtained utilizing a neodymium series catalyst and which exhibits a Mooney viscosity of from about 30 to about 70. The cover composition used in this golf ball includes a combination of three ionomers. That combination includes a sodium ionomer, a magnesium ionomer, and a zinc ionomer.

In a second aspect, the present invention provides a golf ball comprising a core that includes a particular combination of first and second polybutadiene rubbers, in particular weight proportions, and a cover generally enclosing the core which is formed from a certain combination of ionomers. Specifically, the core includes from about 30% by weight of a first polybutadiene rubber obtained from a cobalt or cobalt-based catalyst, and about 30% to about 45% by weight of a second polybutadiene rubber obtained from a neodymium or lanthanide-series catalyst. The cover of the golf ball includes a sodium ionomer, a magnesium ionomer, and a zinc ionomer.

In yet another aspect, the present invention provides a golf ball comprising a core including a certain combination of polybutadiene rubbers, which is enclosed with a cover formed from a particular set of ionomers. The core includes from about 20% to about 30% by weight of a first polyb-

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utadiene rubber obtained from a cobalt catalyst and which exhibits a Mooney viscosity in the range of from about 70 to about 83. The core further includes from about 30% to about 45% of a second polybutadiene rubber obtained from a neodymium catalyst and which exhibits a Mooney viscosity of from about 30 to about 70. The cover which is disposed about the core includes from about 40% to about 50% of a sodium ionomer, from about 40% to about 50% of a magnesium ionomer, and from about 5% to about 15% of a zinc ionomer.

Further scope of the applicability of the invention will become apparent from the detailed description provided below.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a partial sectional view of a first preferred embodiment golf ball in accordance with the present invention.

FIG. 2 is a cross sectional view of the first preferred embodiment golf ball.

FIG. 3 is a partial sectional view of a second preferred embodiment golf ball in accordance with the present invention.

FIG. 4 is a cross sectional view of the second preferred embodiment golf ball.

FIG. 5 is a cross-sectional view of a third preferred embodiment golf ball according to the present invention having a unitary, solid core and a single cover layer.

FIG. 6 is a cross-sectional view of a fourth preferred embodiment of the invention in which the ball has two cover layers.

FIG. 7 is a cross-sectional view of a fifth embodiment of a golf ball according to the present invention in which the ball has a dual layer solid core.

FIG. 8 is a cross-sectional view of a sixth embodiment of the present invention in which the ball has a dual layer solid core and a dual layer cover.

FIG. 9 is a cross-sectional view of an embodiment of the invention in which the ball has a mechanical impedance with a primary minimum value in a particular frequency range.

FIG. 10 is a cross-sectional view of a solid golf ball according to the invention in which the ball has a particular PGA core compression and a mechanical impedance with a primary minimum value in a particular frequency range.

FIG. 11 shows a cross-sectional view of a golf ball according to yet another embodiment of the invention.

FIG. 12 shows a cross-sectional view of a golf ball according to a further embodiment of the invention.

FIG. 13 schematically shows the equipment used to determine mechanical impedance of the golf balls of the present invention.

FIGS. 14-21 are graphs showing mechanical impedance for the golf balls tested in Example 4.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention provides a new, improved class of golf balls. As described herein, these golf balls feature a core comprising a particular combination of butadiene rubbers, and a cover comprising a specific array of ionomer resins.

Cores

The present invention is directed to improved compositions which, when utilized in formulating golf ball cores,

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produce cores that exhibit a relatively high degree of resilience. The invention is also directed to improving the processability of polybutadiene, particularly in forming golf ball cores. In these regards, it has been found that the use of a blend of particular polybutadiene resins in a golf ball core composition has the effect of increasing the resiliency of the resultant cores and greatly facilitates core formation.

The compositions of the present invention comprise one or more rubber or elastomeric components and an array of non-rubber or non-elastomeric components. The rubber components of the core compositions of the invention comprise a particular polybutadiene synthesized with cobalt and having an ultra-high Mooney viscosity and certain molecular weight characteristics described in detail below, one or more particular polybutadienes synthesized with neodymium, and one or more other optional polybutadienes. In some applications, polybutadienes synthesized with nickel catalysts may be used in combination with or instead of polybutadienes synthesized with cobalt catalysts. And, polybutadienes synthesized with lanthanide series catalysts may be used in combination with or instead of polybutadienes synthesized with neodymium catalysts. The non-rubber components of the core compositions of the invention comprise one or more crosslinking agents which preferably include an unsaturated carboxylic acid component, a free radical initiator to promote cross linking, one or more optional modifying agents, fillers, moldability additives, processing additives, and dispersing agents, all of which are described in greater detail below.

The first preferred polybutadiene resin for use in the present invention composition has a relatively ultra high Mooney viscosity. A "Mooney unit" is an arbitrary unit used to measure the plasticity of raw, or unvulcanized rubber. The plasticity in Mooney units is equal to the torque, measured on an arbitrary scale, on a disk in a vessel that contains rubber at a temperature of 212° F. (100° C.) and that rotates at two revolutions per minute.

The measurement of Mooney viscosity, i.e. Mooney viscosity [ML₁₊₄(100° C.)], is defined according to the standard ASTM D-1646, herein incorporated by reference. In ASTM D-1646, it is stated that the Mooney viscosity is not a true viscosity, but a measure of shearing torque over a range of shearing stresses. Measurement of Mooney viscosity is also described in the *Vanderbilt Rubber Handbook*, 13th Ed., (1990), pages 565-566, also herein incorporated by reference. Generally, polybutadiene rubbers have Mooney viscosities, measured at 212° F., of from about 25 to about 65. Instruments for measuring Mooney viscosities are commercially available such as a Monsanto Mooney Viscometer, Model MV 2000. Another commercially available device is a Mooney viscometer made by Shimadzu Seisakusho Ltd.

As will be understood by those skilled in the art, polymers may be characterized according to various definitions of molecular weight. The "number average molecular weight," M_n , is defined as:

$$M_n = \frac{\sum W_i}{\sum W_i / M_i}$$

where W_i is the molecular weight of a fraction or sample of the polymer and M_i is the total number of fractions or samples.

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"Weight average molecular weight," M_w , is defined as:

$$M_w = \frac{\sum W_i M_i}{\sum W_i}$$

where W_i and M_i have the same meanings as noted above. The "Z-average molecular weight," M_z , is defined as:

$$M_z = \frac{\sum W_i M_i^2}{\sum W_i M_i}$$

where W_i and M_i have the same meanings as noted above. " M_{peak} " is the molecular weight of the most common fraction or sample, i.e. having the greatest population.

Considering these various measures of molecular weight, provides an indication of the distribution or rather the "spread" of molecular weights of the polymer under review.

A common indicator of the degree of molecular weight distribution of a polymer is its "polydispersity," P :

$$P = \frac{M_w}{M_n}$$

Polydispersity, also referred to as "dispersity", also provides an indication of the extent to which the polymer chains share the same degree of polymerization. If the polydispersity is 1.0, then all polymer chains must have the same degree of polymerization. Since weight average molecular weight is always equal to or greater than the number average molecular weight, polydispersity, by definition, is equal to or greater than 1.0:

$$P \geq 1.0$$

The first particular polybutadiene for use in the preferred embodiment compositions of the present invention exhibits a Mooney viscosity of from about 65 to about 85, and preferably from about 70 to about 83. The first particular polybutadiene has a number average molecular weight M_n of from about 90,000 to about 130,000; and preferably from about 100,000 to about 120,000. The first particular polybutadiene has a weight average molecular weight M_w of from about 250,000 to about 350,000; and preferably from about 290,000 to about 310,000. The first particular polybutadiene has a Z-average molecular weight M_z of about 600,000 to about 750,000; and preferably from about 660,000 to about 700,000. The first particular polybutadiene has a peak molecular weight M_{peak} of about 150,000 to about 200,000; and preferably from about 170,000 to about 180,000.

The polydispersity of the first particular polybutadiene for use in the preferred embodiment compositions typically ranges from about 1.9 to about 3.9; and preferably from about 2.4 to about 3.1. Most preferably, the polydispersity is about 2.7.

The first particular polybutadiene for use in the preferred embodiment compositions preferably contains a majority fraction of polymer chains containing a cis-1,4 bond, more preferably, having a cis-1,4 polybutadiene content of about 90%, and most preferably, having a cis-1,4 polybutadiene content of at least about 95%. Another characteristic of the first preferred polybutadiene is that it is obtained or synthesized by utilizing a cobalt or cobalt-based catalyst. As noted herein, in some applications, a polybutadiene synthesized by using a nickel catalyst may be employed with, or in place of, the polybutadiene synthesized with a cobalt catalyst.

A commercially available polybutadiene corresponding to the noted first preferred ultra high viscosity polybutadiene,

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and which is suitable for use in the preferred embodiment compositions in accordance with the present invention is available under the designation Cariflex BCP 820, from Shell Chimie of France. Although this polybutadiene produces cores exhibiting higher C.O.R. values, it is somewhat difficult to process using conventional equipment. The properties and characteristics of this preferred polybutadiene are set forth below in Table 1.

TABLE 1

Properties of Shell Chimie BCP 820 (Also Known As BR-1202J)		
Property	Value	
Mooney Viscosity (approximate)	70–83	
Volatiles Content	0.5% maximum	
Ash Content	0.1% maximum	
Cis 1,4-polybutadiene Content	95.0% minimum	
Stabilizer Content	0.2 to 0.3%	
Polydispersity	2.4–3.1	
Molecular Weight Data:	Trial 1	Trial 2
M_n	110,000	111,000
M_w	300,000	304,000
M_z	680,000	
M_{peak}	175,000	

The second polybutadiene for use in the preferred embodiment golf ball core compositions is a polybutadiene that is obtained or synthesized by utilizing a neodymium or lanthanide series catalyst, and that exhibits a Mooney viscosity of from about 30 to about 70, preferably from about 35 to about 70, more preferably from about 40 to about 65, and most preferably from about 45 to about 60. While the second polybutadiene provides covers exhibiting higher C.O.R. values, it exhibits very poor cold flow properties and very high dry swell characteristics.

Examples of such second polybutadienes obtained by using a neodymium-based catalyst include Neo Cis 40, Neo Cis 60 from Enichem and CB-22, CB-23, and CB-24 from Bayer. The properties of these polybutadienes are given below.

TABLE 2

Properties of Neo Cis		
Properties of Raw Polymer		
Microstructure		
1,4 cis (typical)		97.5%
1,4 trans (typical)		1.7%
Vinyl (typical)		0.8%
Volatiles Matter (max)		0.75%
Ash (max)		0.30%
Stabilizer (typical)		0.50%
Mooney Viscosity, ML 1 + 4 at 100° C.	38-48 and 60-66	
Properties of compound (typical)		
Vulcanization at 145° C.		
Tensile strength, 35' cure,	16 MPa	
Elongation, 35' cure,	440%	
300% modulus, 35' cure,	9.5 MPa	

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TABLE 3A

Properties of CB-22			
TESTS	RESULTS	SPECIFICATIONS	
1. Mooney-Viscosity ML1 + 4 100 Cel/ASTM-sheet			
ML1 + 1 Minimum	58		MIN. 58 ME
Maximum	63		MAX. 68 ME
Median	60		58-68 ME
2. Content of ash DIN 53568			
Ash	0.1		MAX. 0.5%
3. Volatile matter heating 3 h/105 Cel			
Loss in weight	0.11		MAX. 0.5%
4. Organic acid Bayer Nr. 18			
Acid	0.33		MAX. 1.0%
5. CIS-1,4 content IR-spectroscopy			
CIS 1,4	97.62		MIN. 96.0%
6. Vulcanization behavior Monsanto MDR/160 Cel DIN 53529			
Compound after			
ts 01	3.2		2.5-4.1 min
t 50	8.3		6.4-9.6 min
t 90	13.2		9.2-14.0 min
s/min	4.2		3.4-4.4 dN.m
s/max	21.5		17.5-21.5 dN.m
7. Informative data			
Vulcanization 150 Cel 30 min			
Tensile	ca. 15.0		
Elongation at break	ca. 450		
Stress at 300% elongation	ca. 9.5		

TABLE 3B

Properties of CB-23			
TESTS	RESULTS	SPECIFICATIONS	
1. Mooney-Viscosity ML1 + 4 100 Cel/ASTM-sheet			
ML1 + 4 Minimum	50		MIN. 46 ME
Maximum	54		MAX. 56 ME
Median	51		46-56 ME
2. Content of ash DIN 53568			
Ash	0.09		MAX. 0.5%
3. Volatile matter DIN 53526			
Loss in weight	0.19		MAX. 0.5%
4. Organic acid Bayer Nr. 18			
Acid	0.33		MAX. 1.0%
5. CIS-1,4 content IR-spectroscopy			
CIS 1,4	97.09		MIN. 96.0%
6. Vulcanization behavior Monsanto MDR/160 Cel DIN 53529			
Compound after			
ts 01	3.4		2.4-4.0 min
t 50	8.7		5.8-9.0 min
t 90	13.5		8.7-13.5 min
s/min	3.1		2.7-3.8 dN.m
s/max	20.9		17.7-21.7 dN.m
7. Vulcanization test with ring			
Informative data			
Tensile	ca. 15.5		
Elongation at break	ca. 470		
Stress at 300% elongation	ca. 9.3		

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TABLE 3C

Properties of CB-24		
TESTS	RESULTS	SPECIFICATIONS
1. Mooney-Viscosity ML1 + 4 100 Cel/ASTM-sheet	44	MIN. 39 ME
ML1 + 4 Minimum	46	MAX. 49 ME
Maximum	45	39-49 ME
Median		
2. Content of ash DIN 53568	0.12	MAX. 0.5%
Ash		
3. Volatile matter DIN 53526	0.1	MAX. 0.5%
Loss in weight		
4. Organic acid Bayer Nr. 18	0.29	MAX. 1.0%
Acid		
5. CIS-1,4 content IR-spectroscopy	96.73	MIN. 96.0%
CIS 1,4		
6. Vulcanization behavior Monsanto MDR/160 Cel		
DIN 53529		
Compound after masticator		
ts 01	3.4	2.6-4.2 min
t 50	8.0	6.2-9.4 min
t 90	12.5	9.6-14.4 min
s'min	2.8	2.0-3.0 dN.m
s'max	19.2	16.3-20.3 dN.m
7. Informative data Vulcanization 150 Cel 30 min		
Tensile	ca. 15.0	
Elongation at break	ca. 470	
Stress at 300% elongation	ca. 9.1	

It has been found that when the first and second polybutadienes are blended together within certain ranges, golf ball cores can be produced without the individual processing difficulties associated with each polybutadiene. In essence, a synergistic effect is produced allowing the blends to produce golf ball cores using conventional equipment exhibiting enhanced resilience.

The compositions of the present invention may also utilize other polybutadiene resins in addition to the noted first and second particular polybutadienes. For example, Cariflex BR-1220 polybutadiene available from Shell Chemical (see Table 4 below); and Taktene 220 polybutadiene available from Bayer Corp. of Orange, Tex. (see Tables 5A and 5B below) may be utilized as other polybutadienes in combination with the particular ultra-high Mooney viscosity polybutadiene components described herein. It is also contemplated that these polybutadienes could be used by themselves and without the particular first and second polybutadienes. Generally, these other polybutadienes have Mooney viscosities in the range of about 25 to 65. It is also contemplated that a similar polybutadiene resin, BCP 819, commercially available from Shell Chimie, may be used in conjunction with BCP 820.

TABLE 4

Properties of Cariflex BR-1220 Polybutadiene	
Physical Properties:	
Polybutadiene Rubber	
CIS 1,4 Content - 97%-99% Min.	
Stabilizer Type - Non Staining	
Total Ash - 0.5% Max.	
Specific Gravity - 0.90-0.92	

TABLE 4-continued

Properties of Cariflex BR-1220 Polybutadiene			
5	Color - Transparent, clear, Lt. Amber		
	Moisture - 0.3% max. ASTM 1416.76 Hot Mill Method		
	Polymer Mooney Viscosity - (35-45 Cariflex) (ML1 + 4 @ 212° F.)		
	90% Cure - 10.0-13.0		
	Polydispersity 2.5-3.5		
10	Molecular Weight Data:	Trial 1	Trial 2
	M_n	80,000	73,000
	M_w	220,000	220,000
	M_z	550,000	
	M_{peak}	110,000	

TABLE 5A

Properties of Taktene 220 Polybutadiene	
Physical Properties:	
20	Polybutadiene Rubber
	CIS 1,4 Content (%) - 98% Typical
	Stabilizer Type - Non Staining 1.0-1.3%
	Total Ash - 0.25 Max.
25	Raw Polymer Mooney Visc. -35-45 40 Typical
	(ML1 + 4' @ 212 Deg. F./212° F.)
	Specific Gravity - 0.91
	Color - Transparent - almost colorless (15 APHA Max.)
	Moisture % - 0.30% Max. ASTM 1416-76 Hot Mill Method

TABLE 5B

Properties of Taktene 220 Polybutadiene			
Product Description	A low Mooney viscosity, non-staining, solution polymerized, high cis-1,4-polybutadiene rubber.		
	Property	Range	Test Method
Raw Polymer Properties	Mooney viscosity 1 + 4 (212° F.)	40 ± 5	ASTM D 1646
	Volatile matter (wt %)	0.3 max.	ASTM D 1416
	Total Ash (wt %)	0.25 max.	ASTM D 1416
Cure ^{(1)(X2)}	Minimum torque		
Characteristics	M_L (dN.m)	9.7 ± 2.2	ASTM D 2084
	(lbf.in)	8.6 ± 1.9	ASTM D 2084
	Maximum torque		
	M_H (dN.m)	35.7 ± 4.8	ASTM D 2084
	(lbf.in)	31.6 ± 4.2	ASTM D 2084
	t_2 1 (min)	4 ± 1.1	ASTM D 2084
	t_{50} (min)	9.6 ± 2.5	ASTM D 2084
	t_{90} (min)	12.9 ± 3.1	ASTM D 2084
	Property	Typical Value	
Other Product Features	Specific gravity	0.91	
	Stabilizer type	Non-staining	

⁽¹⁾Monsanto Rheometer at 160° C., 1.7 Hz (100 cpm), 1 degree arc, micro-die

⁽²⁾Cure characteristics determined on ASTM D 3189 MIM mixed compound:

TAKTENE 220	100 (parts by mass)
Zinc oxide	3
Stearic acid	2
IRB #6 black (N330)	60
Naphthenic oil	15
TBBS	0.9
Sulfur	1.5

*This specification refers to product manufactured by Bayer Corp., Orange, Texas, U.S.A.

Concerning the elastomeric or rubber portion of the preferred embodiment compositions, it is preferred to utilize

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the previously described first and second polybutadienes in particular proportions to one another. Generally, it is preferred to utilize the first polybutadiene in a proportion of less than 50 parts per hundred parts of the total amount of the first and second polybutadienes. Unless indicated otherwise, all parts expressed herein are parts by weight. More preferably, the first polybutadiene is utilized in a proportion of about 45 parts or less (most preferably 40 parts or less) per hundred parts of the total amount of the first and second polybutadienes. With respect to the second polybutadiene, it is generally preferred to utilize the second polybutadiene in a proportion of more than 50 parts per hundred parts of the total amount of the first and second polybutadienes. More preferably, the second polybutadiene is utilized in a proportion of about 55 parts or more (most preferably 60 parts or more) per hundred parts of the total amount of the first and second polybutadienes.

The preferred embodiment core compositions of the present invention generally comprise from about 80 parts to about 120 parts by weight of elastomeric or rubber components, i.e. the first and second polybutadienes, and from about 60 to about 80, or more, parts by weight of non-rubber or non-elastomeric components. Preferably, the core compositions comprise about 100 parts of rubber components and from about 60 to about 80, or more, parts by weight of non-rubber components. It will be understood that depending upon the types and respective function of components added to the non-rubber portion of the preferred embodiment core compositions, that the non-rubber portion may constitute a significant proportion of the rubber component. The rubber components include the previously described first and second polybutadienes. The non-rubber components are as follows.

Preferably, the crosslinking agent of the core composition is an unsaturated carboxylic acid component which is the reaction product of a carboxylic acid or acids and an oxide or carbonate of a metal such as zinc, magnesium, barium, calcium, lithium, sodium, potassium, cadmium, lead, tin, and the like. Preferably, the oxides of polyvalent metals such as zinc, magnesium and cadmium are used, and most preferably, the oxide is zinc oxide.

Exemplary of the unsaturated carboxylic acids which find utility in the preferred core compositions are acrylic acid, methacrylic acid, itaconic acid, crotonic acid, sorbic acid, and the like, and mixtures thereof. Preferably, the acid component is either acrylic or methacrylic acid. Usually, from about 15 to about 50, and preferably from about 20 to about 35 parts by weight of the carboxylic acid salt, such as zinc diacrylate, is included per 100 parts of the rubber components in the core composition. The unsaturated carboxylic acids and metal salts thereof are generally soluble in the elastomeric base, or are readily dispersible.

The free radical initiator included in the core composition is any known polymerization initiator (a co-crosslinking agent) which decomposes during the cure cycle. The term "free radical initiator" as used herein refers to a chemical which, when added to a mixture of the elastomeric blend and a metal salt of an unsaturated, carboxylic acid, promotes crosslinking of the elastomers by the metal salt of the unsaturated carboxylic acid. The amount of the selected initiator present is dictated only by the requirements of catalytic activity as a polymerization initiator. Suitable initiators include peroxides, persulfates, azo compounds and hydrazides. Peroxides which are readily commercially available are conveniently used in the present invention, generally in amounts of from about 0.1 to about 10.0 and preferably in amounts of from about 0.3 to about 3.0 parts by weight per each 100 parts of elastomer.

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Exemplary of suitable peroxides for the purposes of the present invention are dicumyl peroxide, n-butyl 4,4'-bix (butylperoxy) valerate, 1,1-bis (t-butylperoxy)-3,3,5-trimethyl cyclohexane, di-t-butyl peroxide and 2,5-di-(t-butylperoxy)-2,5 dimethyl hexane and the like, as well as mixtures thereof. It will be understood that the total amount of initiators used will vary depending on the specific end product desired and the particular initiators employed.

Examples of such commercial available peroxides are Luperco 230 or 231 XL, a peroxyketal manufactured and sold by Atochem, Lucidol Division, Buffalo, N.Y., and Trigonox 17/40 or 29/40, a peroxyketal manufactured and sold by Akzo Chemie America, Chicago, Ill. The one hour half life of Luperco 231 XL and Trigonox 29/40 is about 112° C., and the one hour half life of Luperco 230 XL and Trigonox 17/40 is about 129° C. Luperco 230 XL and Trigonox 17/40 are n-butyl-4,4-bis(t-butylperoxy) valerate and Luperco 231 XL and Trigonox 29/40 are 1,1-di(t-butylperoxy) 3,3,5-trimethyl cyclohexane. Most preferably, and as noted in Table 6 herein, Trigonox 42-40B from Akzo Nobel of Chicago, Ill. is used. Most preferably, a solid form of this peroxide is used. Trigonox 42-40B is tert-Butyl peroxy-3,5,5-trimethylhexanoate. The liquid form of this agent is available from Akzo under the designation Trigonox 42S.

The core compositions of the present invention may additionally contain any other suitable and compatible modifying ingredients including, but not limited to, metal oxides, fatty acids, and diisocyanates. For example, Papi 94, a polymeric diisocyanate, commonly available from Dow Chemical Co., Midland, Mich., is an optional component in the rubber compositions. It can range from about 0 to 5 parts by weight per 100 parts by weight rubber (phr) component, and acts as a moisture scavenger.

Various activators may also be included in the compositions of the present invention. For example, zinc oxide and/or magnesium oxide are activators for the polybutadiene. The activator can range from about 2 to about 10 parts by weight per 100 parts by weight of the rubbers (phr) component.

Moreover, filler-reinforcement agents may be added to the composition of the present invention. One such example is polypropylene powder. Since the specific gravity of polypropylene powder is very low, and when compounded, the polypropylene powder produces a lighter molded core, large amounts of higher gravity fillers may be added. Additional benefits may be obtained by the incorporation of relatively large amounts of higher specific gravity, inexpensive mineral fillers such as calcium carbonate. Such fillers as are incorporated into the core compositions should be in finely divided form, as for example, in a size generally less than about 30 mesh and preferably less than about 100 mesh U.S. standard size. The amount of additional filler included in the core composition is primarily dictated by weight restrictions and preferably is included in amounts of from about 10 to about 100 parts by weight per 100 parts rubber.

The preferred fillers are relatively inexpensive and heavy and serve to lower the cost of the ball and to increase the weight of the ball to closely approach the U.S.G.A. weight limit of 1.620 ounces. Exemplary fillers include mineral fillers such as limestone, zinc oxide, silica, mica, barytes, calcium carbonate, or clays. Limestone is ground calcium/magnesium carbonate and is used because it is an inexpensive, heavy filler. Other heavy filler include metal particles, such as powdered tungsten, bismuth, or molybdenum. Other filler materials are noted herein.

As indicated, ground flash filler may be incorporated and is preferably 20 mesh ground up center stock from the

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excess flash from compression molding. It lowers the cost and may increase the hardness of the ball.

Fatty acids or metallic salts of fatty acids may also be included in the compositions, functioning to improve moldability and processing. Generally, free fatty acids having from about 10 to about 40 carbon atoms, and preferably having from about 15 to about 20 carbon atoms, are used. Exemplary of suitable fatty acids are stearic acid, palmitic, oleic and linoleic acids, as well as mixtures thereof. Exemplary of suitable metallic salts of fatty acids include zinc stearate. When included in the core compositions, the fatty acid component is present in amounts of from about 1 to about 25, preferably in amounts from about 20 to about 15 parts by weight based on 100 parts rubber (elastomer).

It is preferred that the core compositions include stearic acid as the fatty acid adjunct in an amount of from about 2 to about 5 parts by weight per 100 parts of rubber.

Diisocyanates may also be optionally included in the core compositions when utilized, the diisocyanates are included in amounts of from about 0.2 to about 5.0 parts by weight based on 100 parts rubber. Exemplary of suitable diisocyanates is 4,4'-diphenylmethane diisocyanate and other polyfunctional isocyanates known to the art.

Furthermore, the dialkyl tin difatty acids set forth in U.S. Pat. No. 4,844,471, the dispersing agents disclosed in U.S. Pat. No. 4,838,556, and the dithiocarbonates set forth in U.S. Pat. No. 4,852,884 may also be incorporated into the polybutadiene compositions of the present invention. The specific types and amounts of such additives are set forth in the above-identified patents, which are incorporated herein by reference.

The golf ball core compositions of the invention may also comprise from about 1 to about 100 parts by weight of particulate polypropylene resin, and preferably from about 10 to about 100 parts by weight polypropylene powder resin, per 100 parts by weight of a base elastomer (or rubber) selected from polybutadiene and mixtures of polybutadiene with other elastomers. More preferably, the particulate polypropylene resin, if utilized in the core compositions of the present invention, comprises from about 20 to about 40 parts by weight of a polypropylene powder resin such as that trademarked and sold by Amoco Chemical Co. under the designation "6400 P", "7000P" and "7200 P". The ratios of the ingredients may vary and are best optimized empirically.

As indicated above, additional suitable and compatible modifying agents such as fatty acids, and secondary additives such as Pecan shell flour, ground flash (i.e. grindings from previously manufactured cores of substantially identical construction), barium sulfate, zinc oxide, etc. may be added to the core compositions to increase the weight of the ball as necessary in order to have the ball reach or closely approach the U.S.G.A. weight limit of 1.620 ounces.

Most preferably, a core formulation in accordance with the present invention is as follows in Table 6:

TABLE 6

Ingredients	Parts	Wt %
Cariflex 1220x (BCP-820)	40	24.64
Neo Cis 60	30	18.48
Neo Cis 40	30	18.48
Zinc Oxide	24	14.78
Tungsten powder	0.17	0.105
Zinc Stearate	16.3	10.04
Zinc Diacrylate (ZDA)	20.5	12.63
Red MB	0.14	0.086

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TABLE 6-continued

Ingredients	Parts	Wt %
Triganox 42-40B	1.24	0.76
Total	162.4	100

In this preferred core formulation, it will be noted that the weight ratio of the polybutadiene formed from the cobalt catalyst (Cariflex BCP-820) to the polybutadiene formed from the neodymium catalyst (Neo Cis 60 and Neo Cis 40) is about 2:3. The present invention includes a wide range of such ratios, such as from 1:10 to 10:1. Preferably, the amount of the cobalt catalyst polybutadiene ranges from about 20% to about 30% of the core formulation. And, preferably, the amount of the neodymium catalyst polybutadiene ranges from about 30% to about 45% of the core formulation. Most preferably, these polybutadienes are in amounts of 25% and 37%, respectively.

It will be understood that the present invention golf balls may further include one or more interior or mantle layers. Such layers are usually disposed between the core and the cover components of the ball. It is also contemplated that the preferred blend of first and second polybutadienes described herein could be utilized in one or more of these interior mantle layers.

The present invention is well suited for forming cores for golf balls as described herein. Referring to FIGS. 1 and 2, a first preferred embodiment golf ball 10 is illustrated. It will be understood that all figures are schematics and not necessarily to scale. The first preferred embodiment golf ball 10 comprises a core 20, most preferably as described herein, and a cover layer 30 disposed about the core 20. The core 30 includes an outer surface 35 that defines a plurality of dimples 40 along the outer surface 35 as is known in the art.

The present invention core compositions are also well suited for use in multi-layer golf balls such as for example, a second preferred golf ball 50 illustrated in FIGS. 3 and 4. The second preferred embodiment golf ball 50 comprises a core 60, a first inner layer 70 disposed about the core 60, and an outer cover layer 80 disposed about the inner layer 70. The inner layer 70 may include one or more interior layers or mantles. The outer cover layer 80 may include one or more cover layers. The outer layer 80 includes an outer surface 85 that defines a plurality of dimples 90 as known in the art.

In producing golf ball cores utilizing the present compositions, the ingredients may be intimately mixed using, for example, two roll mills or a Banbury mixer until the composition is uniform, usually over a period of from about 5 to about 20 minutes. The sequence of addition of components is not critical. A preferred blending sequence is as follows.

The elastomer, powder resin, fillers, zinc salt, metal oxide, fatty acid, and any other optional components, if desired, are blended for about 7 minutes in an internal mixer such as a Banbury mixer. As a result of shear during mixing, the temperature rises to about 200° F., whereupon the batch is discharged onto a two roll mill, mixed for about one minute and sheeted out.

The sheet is then placed in a Barwell preformer and slugs are produced. The slugs are then subjected to compression molding at about 320° F. for about 14 minutes. After molding and cooling, the cooling effected at room temperature for about 4 hours, the molded cores are subjected to a centerless grinding operation whereby a thin layer of the

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molded core is removed to produce a round core having a diameter of 1.545 inches.

The mixing is desirably conducted in such a manner that the composition does not reach incipient polymerization temperatures during the blending of the various components.

Usually the curable component of the composition will be cured by heating the composition at elevated temperatures on the order of from about 275° F. to about 350° F., preferably and usually from about 290° F. to about 325° F., with molding of the composition effected simultaneously with the curing thereof. The composition can be formed into a core structure by any one of a variety of molding techniques, e.g. injection, compression, or transfer molding. When the composition is cured by heating, the time required for heating will normally be short, generally from about 10 to about 20 minutes, depending upon the particular curing agent used. Those of ordinary skill in the art relating to free radical curing agents for polymers are conversant with adjustments of cure times and temperatures required to effect optimum results with any specific free radical agent.

After molding, the core is removed from the mold and the surface thereof, preferably treated to facilitate adhesion thereof to the covering materials. Surface treatment can be effected by any of the several techniques known in the art, such as corona discharge, ozone treatment, sand blasting, and the like. Preferably, surface treatment is effected by grinding with an abrasive wheel.

The core is converted into a golf ball by providing at least one layer of covering material thereon, ranging in thickness from about 0.050 to about 0.250 inch and preferably from about 0.060 to about 0.090 inch.

Covers

The cover layers can be formed over the cores by injection molding, compression molding, casting or other conventional molding techniques. Each layer preferably is separately formed. It is preferable to form each layer by either injection molding or compression molding. A more preferred method of making a golf ball of the invention with a multi-layer cover is to successively injection mold each layer in a separate mold. First, the inner cover layer is injection molded over the core in a smooth cavity mold, subsequently any intermediate cover layers are injection molded over the inner cover layer in a smooth cavity mold, and finally the outer cover layer is injection molded over the intermediate cover layers in a dimpled cavity mold.

The outer cover layer of the golf ball of the present invention is based on a resin material. Non-limiting examples of suitable materials are ionomers, plastomers such as metallocene catalyzed polyolefins, e.g., EXACT, ENGAGE, INSITE or AFFINITY which preferably are cross-linked, polyamides, amide-ester elastomers, graft copolymers of ionomer and polyamide such as CAPRON, ZYTEL, PEBAX, etc., blends containing cross-linked transpolyisoprene, thermoplastic block polyesters such as HYTREL, or thermoplastic or thermosetting polyurethanes, and polyureas such as ESTANE, which is thermoplastic.

Any inner cover layers which are part of the ball can be made of any of the materials listed in the previous paragraph as being useful for forming an outer cover layer. Furthermore, any inner cover layers can be formed from a number of other non-ionomeric thermoplastics and thermosets. For example, lower cost polyolefins and thermoplastic elastomers can be used. Non-limiting examples of suitable non-ionomeric polyolefin materials include low density polyethylene, linear low density polyethylene, high density polyethylene, polypropylene, rubber-toughened olefin

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polymers, acid copolymers which do not become part of an ionomeric copolymer when used in the inner cover layer, such as PRIMACOR, NUCREL, ESCOR and ATX, flexomers, thermoplastic elastomers such as styrenebutadiene/styrene (SBS) or styrene/ethylene-butylene/styrene (SEBS) block copolymers, including Kraton (Shell), dynamically vulcanized elastomers such as Santoprene (Monsanto), ethylene vinyl acetates such as Elvax (DuPont), ethylene methyl acrylates such as Optema (Exxon), polyvinyl chloride resins, and other elastomeric materials may be used. Mixtures, blends, or alloys involving the materials described above can be used. It is desirable that the material used for the inner cover layer be a tough, low density material. The non-ionomeric materials can be mixed with ionomers.

The outer cover layer and any inner cover layers optionally may include processing aids, release agents and/or diluents. Another useful material for any inner cover layer or layers is a natural rubber latex (prevulcanized) which has a tensile strength of 4,000–5,000 psi, high resilience, good scuff resistance, a Shore D hardness of less than 15 and an elongation of 500%.

When the ball has a single cover layer, it has a thickness of 0.010–0.500 inches, preferably 0.015–0.200 inches, and more preferably 0.025–0.150 inches. When the ball has two or more cover layers, the outer cover layer typically has a thickness of 0.01–0.20 inches, preferably 0.02–0.20 inches, and more preferably 0.025–0.15 inches. The one or more inner cover layers have thicknesses appropriate to result in an overall cover thickness of 0.03–0.50 inches, preferably 0.05–0.30 inches and more preferably 0.10–0.20 inches, with the minimum thickness of any single inner cover layer preferably being 0.01 inches.

The core and/or cover layers of the golf ball optionally can include fillers to adjust, for example, flex modulus, density, mold release, and/or melt flow index. A description of suitable fillers is provided below in the "Definitions" section.

The physical characteristics of the cover are such that the ball has a soft feel. When a single cover layer is used, the Shore D hardness of that cover layer is at least 60 in one preferred form of the invention. When the ball has a multi-layer cover, the Shore D hardness of the outer cover layer is at least 60 in another preferred form of the invention. Preferably, the outer cover layer in a single or multi-layer covered ball has a Shore D hardness of at least 63, more preferably at least 65, and most preferably at least 67. The preferred maximum Shore D hardness for the outer cover layer is 90.

A particularly preferred embodiment of an outer cover layer for use in forming the golf ball of the present invention incorporates high molecular weight ionomer resins, such as EX 1005, 1006, 1007, 1008 and 1009, provided by Exxon Chem. Co., or any combination thereof, as shown in Table 7. These resins are particularly useful in forming the outer cover layer because they have a tensile modulus/hardness ratio that allows for a hard cover over a soft core while maintaining durability.

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TABLE 7

Examples of Exxon High Molecular Weight Ionomers						
PROPERTY	Ex 1006	Ex 1006	Ex 1007	Ex 1008	Ex 1009	7310
Melt Index, g/10 min.	0.7	1.3	1.0	1.4	0.8	1.0
Cation	Na	Na	Zn	Zn	Na	Zn
Melting Point, ° C.	85.3	86	85.8	86	91.3	91
Vicat Softening Point, ° C.	54	57	60.5	60	56	69
Tensile @ Break, MPa	33.9	33.5	24.1	23.6	32.4	24
Elongation @ Break, %	403	421	472	427	473	520
Hardness, Shore D	58	58	51	50	56	52
Flexural Modulus, MPa	289	290	152	141	282	150

Appropriate fillers or additive materials may also be added to produce the cover compositions of the present invention. These additive materials include dyes (for example, Ultramarine Blue sold by Whitaker, Clark and Daniels of South Plainfield, N.J.), and pigments, i.e., white pigments such as titanium dioxide (for example UNITANE 0-110 commercially available from Kemira, Savannah, Ga.) zinc oxide, and zinc sulfate, as well as fluorescent pigments. As indicated in U.S. Pat. No. 4,884,814, the amount of pigment and/or dye used in conjunction with the polymeric cover composition depends on the particular base ionomer mixture utilized and the particular pigment and/or dye utilized. The concentration of the pigment in the polymeric cover composition can be from about 1% to about 10% as based on the weight of the base ionomer mixture. A more preferred range is from about 1% to about 5% as based on the weight of the base ionomer mixture. The most preferred range is from about 1% to about 3% as based on weight of the base ionomer mixture. The most preferred pigment for use in accordance with this invention is titanium dioxide (Anatase).

Moreover, since there are various hues of white, i.e. blue white, yellow white, etc., trace amounts of blue pigment may be added to the cover stock composition to impart a blue white appearance thereto. However, if different hues of the color white are desired, different pigments can be added to the cover composition at the amounts necessary to produce the color desired.

In addition, it is within the purview of this invention to add to the cover compositions of this invention compatible materials which do not affect the basic novel characteristics of the composition of this invention. Among such materials are antioxidants (i.e. Santonox R), commercially available from Flexsys, Akron, Ohio, antistatic agents, stabilizers, compatibilizers and processing aids. The cover compositions of the present invention may also contain softening agents, such as plasticizers, etc., and reinforcing materials, as long as the desired properties produced by the golf ball covers of the invention are not impaired.

Furthermore, optical brighteners, such as those disclosed in U.S. Pat. No. 4,679,795 may also be included in the cover composition of the invention. Examples of suitable optical brighteners which can be used in accordance with this invention are Uvitex OB as sold by the Ciba-Geigy Chemical Company, Ardsley, N.Y. Uvitex OB is believed to be 2,5-Bis(5-tert-butyl-2-benzoxazolyl)-thiophene. Examples of other optical brighteners suitable for use in accordance with this invention are as follows: Leucopure EGM as sold

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by Sandoz, East Hanover, N.J. 07936. Leucopure EGM is thought to be 7-(2n-naphthol(1,2-d)-triazol-2yl(3phenyl)-coumarin. Phorwhite K-20G2 is sold by Mobay Chemical Corporation, P.O. Box 385, Union Metro Park, Union, N.J. 07083, and is thought to be a pyrazoline derivative. Eastobrite OB-1 as sold by Eastman Chemical Products, Inc., Kingsport, Tenn. is thought to be 4,4-Bis(-benzoxazolyl) stilbene. The above-mentioned UVITEX and EASTOBRITE OB-1 are preferred optical brighteners for use in accordance with this invention.

Moreover, since many optical brighteners are colored, the percentage of optical brighteners utilized must not be excessive in order to prevent the optical brightener from functioning as a pigment or dye in its own right.

The percentage of optical brighteners which can be used in accordance with this invention is from about 0.01% to about 0.5% as based on the weight of the polymer used as a cover stock. A more preferred range is from about 0.05% to about 0.25% with the most preferred range from about 0.10% to about 0.20% depending on the optical properties of the particular optical brightener used and the polymeric environment in which it is a part.

Generally, the additives are admixed with an ionomer to be used in the cover composition to provide a masterbatch (abbreviated herein as MB) of desired concentration and an amount of the masterbatch sufficient to provide the desired amounts of additive is then admixed with the copolymer blends.

Most preferably, the preferred embodiment golf balls of the present invention utilize a particular cover composition in combination with a core having a particular set of physical properties. The formulation of this most preferred core is set forth in Table 6. This most preferred golf ball is as follows in Tables 8A and 8B set forth below.

TABLE 8A

Core Data	
Size	1.56" +/- 0.005
Weight	38.0 g +/- 0.004
Riehle Comp	113 +/- 9
COR	0.780 +/- 0.010
Specific Gravity	1.16
JIS C	73 +/- 1
Shore C	75 +/- 2
Shore D	44 +/- 1
Final Ball Data	
Cover Composition	
Iotek 1006/8610 (Na)	45.15
Surllyn 8552/6120 (Mg)	45.15
Iotek 7030 (Zn)	9.7
Whitener Package	3.1 phr
Flex Modulus (weighted avg)	379 MPa
Cover Specific Gravity	0.98 +/- 0.01
Size	1.685" +/- 0.005
Weight	45.4 g +/- 0.4
Riehle Comp	95 +/- 5
COR	0.806 +/- 0.009
JIS C	95 +/- 1
Shore C	97 +/- 1
Shore D	69 +/- 1

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TABLE 8B

Ionomers in Cover			
Individual Ionomers			
	Iotek 1006/8610	Surlyn 8552/6120	Iotek 7030
% Acid/Type ¹	15% AA	19% MA	15% AA
Ionomer Type	Copolymer	Copolymer	Copolymer
Cation	Na	Mg	Zn
Melt Index	1.3	1.3	2.5
Stiffness	2719 Kgf/cm ²	3499 Kgf/cm ²	1840 Kgf/cm ²
Modulus ²			
Flex Modulus	290 MPa	517 MPa	155 MPa

¹AA = Acrylic Acid, MA = Methacrylic Acid²Stiffness measurements done using Toyoseiki Stiffness Tester

Details of the individual components of this most preferred cover composition are set forth below in Tables 9A-9C.

TABLE 9A

Iotek 8610 Ethylene Acrylic Acid Sodium Ionomer			
Description			
Iotek 8610 is a low melt index sodium ionomer made from an ethylene acrylic acid base polymer. It is designed to have high durability, resilience and impact strength.			
	ASTM Method	Units (SI)	Typical Value ¹
Resin Properties			
Melt Index	D-1238 ³	g/10 min.	1.3
Cation	Exxon Method	—	Na
Density	D-1505	g/cm ³	0.951
Melting Point	D-3417	° F. (° C.)	187 (86)
Physical Properties ²			
Tensile Strength @ Break	D-638	psi (MPa)	4930 (34)
Ultimate Elongation	D-638	%	420
Flexural Modulus,	D-790	psi (MPa)	42,000 (290)
1% Secant			
Vicat Softening Point	D-1525 (Rate B)	° F. (° C.)	135 (57)
Hardness Shore D	D-2240	—	58

¹Values given above are typical.²Tensile testing was performed on Type IV compression molded specimens.³Run at 190° C. with 2.16 kg load.

TABLE 9B

Surlyn ® 6120 Resin			
Description			
Surlyn ® 6120 is a magnesium ionomer that provides good toughness, high stiffness and durability. It is positioned in the high acid, medium neutralization area of the ionomer spectrum.			
Typical Properties of Surlyn ® 6120	Units	ASTM Method	Surlyn 6120
General			
Cation Type			Mg
Melt Flow Index	g/10 min	D-1238	1.3

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TABLE 9B-continued

Surllyn ® 6120 Resin				
5	Specific Gravity		D-792	0.95
	<u>Mechanical</u>			
	Tensile Strength	kpsi (MPa)	D-638	5.2 (35.9)
	Yield Strength	kpsi (MPa)	D-638	2.9 (20.0)
	Elongation	%	D-638	270
10	Hardness	D	D-2240	67
	Flexural Modulus	kpsi (MPa)	D-790 (B)	75 (517)
	<u>Thermal</u>			
	Melt Point	° F. (° C.)	D-3418 (DSC)	185 (85)
	Freeze Point	° F. (° C.)	D-3418 (DSC)	102 (39)
15	Vicat Softening Point	° F. (° C.)	D-1525	140 (60)

TABLE 9C

<u>Iotek 7030</u>				
	Test Method	Unit	Typical Value	
<u>Physical Property</u>				
25	Melt Index	ASTM D 1238	g/10 min.	2.5
	Density	ASTM D 1505	kg/m ³	964
	Cation type			zinc
	Melting point (DSC)	ASTM D 3417	° C.	85
	Crystallization point (DSC)	ASTM D 3417	° C.	58
30	Plaque properties (2 mm thickness, compression molded)			
	Tensile strength at break	ASTM D 638	MPa	22.6
	Yield strength	ASTM D 638	MPa	12
	Elongation at break	ASTM D 638	%	460
35	1% secant modulus	ASTM D 638	MPa	125
	Vicat softening point	ASTM D 1525	° C.	60
	Hardness Shore D	ASTM D 2240		52
	Abrasion resistance (weight loss)	ASTM D 1242	mg	25
	Tensile Impact at 23° C. at -40° C.	ASTM D 1822	kJ/m ²	480 340
40	Flexural modulus (3 mm)	ASTM D 790	MPa	155
	De Mattia flex resistance	ASTM D 430	Cycles	>5000
	Zwick rebound	DIN 53512	%	40

It will be noted that this most preferred cover formulation includes the combination of a sodium ionomer, a magnesium ionomer, and a zinc ionomer. The amounts of each of these may be tailored as desired, however the preferred amounts are as followed. The sodium ionomer is preferably employed within the range of from about 40% to about 50% of the cover formulation, and most preferably at about 45%. The magnesium ionomer is preferably used within the range of from about 40% to about 50% of the cover formulation, and most preferably at about 45%. The zinc ionomer is preferably used within the range of from about 5% to about 15%, and most preferably at about 10%.

The golf ball of the present invention preferably has a mechanical impedance with a primary minimum value in the frequency range of 3100 Hz or less, and preferably 100-3100 Hz. This low mechanical impedance provides the ball with a soft feel. This soft feel in combination with excellent distance provide a golf ball which is particularly well suited for use by intermediate players who like a soft ball but desire a greater distance than can be achieved with a conventional balata ball.

Mechanical impedance is defined as the ratio of magnitude and force acting at a particular point to a magnitude of

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a responsive velocity at another point when the force is acted. Stated another way, mechanical impedance Z is given by $Z=FN$, where F is an externally applied force and V is a responsive velocity of the object to which the force is applied. The velocity V is the internal velocity of the object.

Mechanical impedance and natural frequency can be depicted graphically by plotting impedance on the "Y" axis and frequency N (Hz) on the "X" axis. A graph of this type is shown in FIGS. 14-21.

As shown in FIG. 14, a golf ball of Example 2 which is analyzed in Example 4 has a mechanical impedance with a primary minimum value at a first frequency, a mechanical impedance with a secondary minimum value at a higher frequency, and a third minimum value at an even higher frequency. These are known as the primary, secondary and tertiary minimum frequencies. The first minimum value which appears on the graph is not the primary minimum frequency of the ball but instead represents the forced node resonance of the ball due to the introduction of an artificial node, such as a golf club. The forced node resonance is a frequency which may depend in part upon the nature of the artificial node. The existence of forced node resonance is analogous to the change in frequency which is obtained on a guitar by placing a finger over a fret.

The mechanical impedance can be measured using an accelerometer. Further details regarding natural frequency determinations are provided below in the Examples.

Referring to FIG. 5, a third embodiment of a golf ball according to present invention is shown and is designated as 110. The ball includes a central core 112 formed from polybutadiene or another cross-linked rubber. A cover layer 114 surrounds the core. The core has a PGA compression of 55 or less. The cover has a Shore D hardness of at least 60. The ball has a PGA compression of 80 or less.

Referring now to FIG. 6, a cross-sectional view of a fourth embodiment of the invention is shown, and is designated as 120. The ball 120 has a solid core 122, an inner cover layer 124, and an outer cover layer 126. The core has a PGA compression of 55 or less. The outer cover layer has a Shore D hardness of 60 or more. The inner cover layer can be softer or harder than the outer cover layer, but provides the overall ball with a PGA compression of 80 or less.

A fifth embodiment of a golf ball according to the present invention is shown in FIG. 7, and is designated as 130. The ball includes a solid core 131 which is formed from two layers, namely, an inner core layer 132 and an outer core layer 133. A cover 134 surrounds the core 131. The inner core layer 132 and outer core layer 133 are selected to provide the overall core 131 with a PGA compression of 55 or less. The inner core layer may be harder or softer than the outer core layer and may also be higher in durability. The cover has a Shore D hardness of at least 60. The ball has a PGA compression of 80 or less.

FIG. 8 shows a cross-sectional view of a sixth embodiment of a golf ball according to the present invention, which is designated as 140. The ball includes a core 141 having an inner core layer 142 and an outer core layer 143. A dual layer cover 144 surrounds the core 141. The dual layer cover 144 includes an inner cover layer 145 and an outer cover layer 146. The core 141 has a PGA compression of 55 or less. The outer cover layer 146 has a Shore D hardness of 60 or more. The ball has a PGA compression of 80 or less.

FIG. 9 shows yet another preferred embodiment of the present invention, which is designated as 150. The ball 150 has a core 152 formed from one or more layers and a cover 154 formed from one or more layers. The ball is constructed

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such that the outer cover layer has a Shore D hardness of at least 60, and the ball has a mechanical impedance with a primary minimum value in the frequency range of 3100 Hz, after the ball has been maintained at 21.1° C., 1 atm. and about 50% relative humidity for at least 15 hours.

Yet another embodiment of a golf ball according to the invention is shown in FIG. 10 and is designated as 160. The ball has a solid core 162 and a cover 164, each of which can be formed of one or more layers. The core 162 has a PGA compression of 55 or less and the cover has a Shore D hardness of at least 58. The ball has a mechanical impedance with a primary minimum value in the frequency range of 3100 Hz or less after the ball has been maintained at 21.1° C., 1 atm. and about 50% relative humidity for at least 15 hours.

Yet another embodiment of a golf ball according to the invention is shown in FIG. 11. The ball 170 includes a solid or wound core 172 and a cover 174. Each of the core and cover can have one or more layers. The outer cover layer of the ball has a Shore D hardness of at least 60. The ball has a mechanical impedance with a primary minimum value in the frequency range of 2600 or less after the ball has been maintained at 21.1, 1 atm. and about 50% relative humidity for at least 15 hours.

Yet another preferred form of the invention is shown in FIG. 12 and is designated as 180. The ball 180 has a core 182 which can be solid or wound, and a cover 184. The ball includes a core 182 which can be solid or wound, and can have one or more layers, and a cover 184 which can have one or more layers. The core has a PGA compression of 55 or less. The ball has a mechanical impedance with a primary minimum value in the frequency range of 2600 Hz or less after the ball has been maintained at 21.1° C., 1 atm. and about 50% relative humidity for at least 15 hours.

The composition of the cover may vary depending upon the desired properties for the resulting golf ball. A wide array of cover formulations may be utilized such as those disclosed in U.S. Pat. Nos. 4,986,545; 5,098,105; 5,120,791; 5,187,013; 5,306,760; 5,312,857; 5,324,783; 5,328,959; 5,330,837; 5,338,610; 5,542,677; 5,580,057; 5,591,803; and 5,733,206, all of which are hereby incorporated by reference.

The covered golf ball can be formed in any one of several methods known in the art. For example, the molded core may be placed in the center of a golf ball mold and the ionomeric resin-containing cover composition injected into and retained in the space for a period of time at a mold temperature of from about 40° F. to about 120° F.

Alternatively, the cover composition may be injection molded at about 300° F. to about 450° F. into smooth-surfaced hemispherical shells, a core and two such shells placed in a dimpled golf ball mold and unified at temperatures on the order of from about 200° F. to about 300° F.

The golf ball produced is then painted and marked, painting being effected by spraying techniques.

DEFINITIONS

The following is a series of definitions used in the specification and claims.

PGA Compression

PGA compression is an important property involved in the performance of a golf ball. The compression of the ball can affect the playability of the ball on striking and the sound or "click" produced. Similarly, compression can effect the

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"feel" of the ball (i.e., hard or soft responsive feel), particularly in chipping and putting.

Moreover, while compression itself has little bearing on the distance performance of a ball, compression can affect the playability of the ball on striking. The degree of compression of a ball against the club face and the softness of the cover strongly influences the resultant spin rate. Typically, a softer cover will produce a higher spin rate than a harder cover. Additionally, a harder core will produce a higher spin rate than a softer core. This is because at impact a hard core serves to compress the cover of the ball against the face of the club to a much greater degree than a soft core thereby resulting in more "grab" of the ball on the clubface and subsequent higher spin rates. In effect the cover is squeezed between the relatively incompressible core and clubhead. When a softer core is used, the cover is under much less compressive stress than when a harder core is used and therefore does not contact the clubface as intimately. This results in lower spin rates.

The term "compression" utilized in the golf ball trade generally defines the overall deflection that a golf ball undergoes when subjected to a compressive load. For example, PGA compression indicates the amount of change in golf ball's shape upon striking. The development of solid core technology in two-piece balls has allowed for much more precise control of compression in comparison to thread wound three-piece balls. This is because in the manufacture of solid core balls, the amount of deflection or deformation is precisely controlled by the chemical formula used in making the cores. This differs from wound three-piece balls wherein compression is controlled in part by the winding process of the elastic thread. Thus, two-piece and multi-layer solid core balls exhibit much more consistent compression readings than balls having wound cores such as the thread wound three-piece balls.

In the past, PGA compression related to a scale of from 0 to 200 given to a golf ball. The lower the PGA compression value, the softer the feel of the ball upon striking. In practice, tournament quality balls have compression ratings around 70-110, preferably around 80 to 100.

In determining PGA compression using the 0-200 scale, a standard force is applied to the external surface of the ball. A ball which exhibits no deflection (0.0 inches in deflection) is rated 200 and a ball which deflects $\frac{1}{16}$ th of an inch (0.2 inches) is rated 0. Every change of 0.001 of an inch in deflection represents a 1 point drop in compression. Consequently, a ball which deflects 0.1 inches (100x0.001 inches) has a PGA compression value of 100 (i.e., 200-100) and a ball which deflects 0.110 inches (110x0.001 inches) has a PGA compression of 90 (i.e., 200-110).

In order to assist in the determination of compression, several devices have been employed by the industry. For example, PGA compression is determined by an apparatus fashioned in the form of a small press with an upper and lower anvil. The upper anvil is at rest against a 200-pound die spring, and the lower anvil is movable through 0.300 inches by means of a crank mechanism. In its open position the gap between the anvils is 1.780 inches allowing a clearance of 0.100 inches for insertion of the ball. As the lower anvil is raised by the crank, it compresses the ball against the upper anvil, such compression occurring during the last 0.200 inches of stroke of the lower anvil, the ball then loading the upper anvil which in turn loads the spring. The equilibrium point of the upper anvil is measured by a dial micrometer if the anvil is deflected by the ball more than 0.100 inches (less deflection is simply regarded as zero

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compression) and the reading on the micrometer dial is referred to as the compression of the ball. In practice, tournament quality balls have compression ratings around 80 to 100 which means that the upper anvil was deflected a total of 0.120 to 0.100 inches.

An example to determine PGA compression can be shown by utilizing a golf ball compression tester produced by Atti Engineering Corporation of Newark, N.J. The value obtained by this tester relates to an arbitrary value expressed by a number which may range from 0 to 100, although a value of 200 can be measured as indicated by two revolutions of the dial indicator on the apparatus. The value obtained defines the deflection that a golf ball undergoes when subjected to compressive loading. The Atti test apparatus consists of a lower movable platform and an upper movable spring-loaded anvil. The dial indicator is mounted such that it measures the upward movement of the spring-loaded anvil. The golf ball to be tested is placed in the lower platform, which is then raised a fixed distance. The upper portion of the golf ball comes in contact with and exerts a pressure on the springloaded anvil. Depending upon the distance of the golf ball to be compressed, the upper anvil is forced upward against the spring.

Alternative devices have also been employed to determine compression. For example, Applicant also utilizes a modified Riehle Compression Machine originally produced by Riehle Bros. Testing Machine Company, Phil., Pa. to evaluate compression of the various components (i.e., cores, mantle cover balls, finished balls, etc.) of the golf balls. The Riehle compression device determines deformation in thousandths of an inch under a load designed to emulate the 200 pound spring constant of the Atti or PGA compression device. Using such a device, a Riehle compression of 61 corresponds to a deflection under load of 0.061 inches.

Additionally, an approximate relationship between Riehle compression and PGA compression exists for balls of the same size. It has been determined by Applicant that Riehle compression corresponds to PGA compression by the general formula $\text{PGA compression} = 160 - \text{Riehle compression}$. Consequently, 80 Riehle compression corresponds to 80 PGA compression, 70 Riehle compression corresponds to 90 PGA compression, and 60 Riehle compression corresponds to 100 PGA compression. For reporting purposes, Applicant's compression values are usually measured as Riehle compression and converted to PGA compression.

Furthermore, additional compression devices may also be utilized to monitor golf ball compression so long as the correlation to PGA compression is known. These devices have been designed, such as a Whitney Tester, to correlate or correspond to PGA compression through a set relationship or formula.

Coefficient of Restitution

The resilience or coefficient of restitution (COR) of a golf ball is the constant "e," which is the ratio of the relative velocity of an elastic sphere after direct impact to that before impact. As a result, the COR ("e") can vary from 0 to 1, with 1 being equivalent to a perfectly or completely elastic collision and 0 being equivalent to a perfectly or completely inelastic collision.

COR, along with additional factors such as club head speed, club head mass, ball weight, ball size and density, spin rate, angle of trajectory and surface configuration (i.e., dimple pattern and area of dimple coverage) as well as environmental conditions (e.g. temperature, moisture, atmospheric pressure, wind, etc.) generally determine the dis-

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tance a ball will travel when hit. Along this line, the distance a golf ball will travel under controlled environmental conditions is a function of the speed and mass of the club and size, density and resilience (COR) of the ball and other factors. The initial velocity of the club, the mass of the club and the angle of the ball's departure are essentially provided by the golfer upon striking. Since club head, club head mass, the angle of trajectory and environmental conditions are not determinants controllable by golf ball producers and the ball size and weight are set by the U.S.G.A., these are not factors of concern among golf ball manufacturers. The factors or determinants of interest with respect to improved distance are generally the coefficient of restitution (COR) and the surface configuration (dimple pattern, ratio of land area to dimple area, etc.) of the ball.

The COR in solid core balls is a function of the composition of the molded core and of the cover. The molded core and/or cover may be comprised of one or more layers such as in multi-layered balls. In balls containing a wound core (i.e., balls comprising a liquid or solid center, elastic windings, and a cover), the coefficient of restitution is a function of not only the composition of the center and cover, but also the composition and tension of the elastomeric windings. As in the solid core balls, the center and cover of a wound core ball may also consist of one or more layers.

The coefficient of restitution is the ratio of the outgoing velocity to the incoming velocity. In the examples of this application, the coefficient of restitution of a golf ball was measured by propelling a ball horizontally at a speed of 125 \pm 5 feet per second (fps) and corrected to 125 fps against a generally vertical, hard, flat steel plate and measuring the ball's incoming and outgoing velocity electronically. Speeds were measured with a pair of Oehler Mark 55 ballistic screens available from Oehler Research, Inc., P.O. Box 9135, Austin, Tex. 78766, which provide a timing pulse when an object passes through them. The screens were separated by 36" and are located 25.25" and 61.25" from the rebound wall. The ball speed was measured by timing the pulses from screen 1 to screen 2 on the way into the rebound wall (as the average speed of the ball over 36"), and then the exit speed was timed from screen 2 to screen 1 over the same distance. The rebound wall was tilted 2 degrees from a vertical plane to allow the ball to rebound slightly downward in order to miss the edge of the cannon that fired it. The rebound wall is solid steel 2.0 inches thick.

As indicated above, the incoming speed should be 125 \pm 5 fps but corrected to 125 fps. The correlation between COR and forward or incoming speed has been studied and a correction has been made over the \pm 5 fps range so that the COR is reported as if the ball had an incoming speed of exactly 125.0 fps.

The coefficient of restitution must be carefully controlled in all commercial golf balls if the ball is to be within the specifications regulated by the United States Golf Association (U.S.G.A.). As mentioned to some degree above, the U.S.G.A. standards indicate that a "regulation" ball cannot have an initial velocity exceeding 255 feet per second in an atmosphere of 75° F. when tested on a U.S.G.A. machine. Since the coefficient of restitution of a ball is related to the ball's initial velocity, it is highly desirable to produce a ball having sufficiently high coefficient of restitution to closely approach the U.S.G.A. limit on initial velocity, while having an ample degree of softness (i.e., hardness) to produce enhanced playability (i.e., spin, etc.).

Shore D Hardness

As used herein, "Shore D hardness" of a cover layer is measured generally in accordance with ASTM D-2240,

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except the measurements are made on the curved surface of a molded cover layer, rather than on a plaque. Furthermore, the Shore D hardness of the cover layer is measured while the cover layer remains over the core and any underlying cover layers. When a hardness measurement is made on a dimpled cover, Shore D hardness is measured, to the best extent possible, at a land area of the dimpled cover.

Plastomers

Plastomers are polyolefin copolymers developed using metallocene single-site catalyst technology. Polyethylene plastomers generally have better impact resistance than polyethylenes made with Ziegler-Natta catalysts. Plastomers exhibit both thermoplastic and elastomeric characteristics. In addition to being comprised of a polyolefin such as ethylene, plastomers contain up to about 35 wt % comonomer. Plastomers include but are not limited to ethylene-butene copolymers, ethylene-octene copolymers, ethylene-hexene copolymers, and ethylene-hexene-butene terpolymers, as well as mixtures thereof.

The plastomers which are useful in the invention preferably are formed by a single site metallocene catalyst such as those disclosed in EP 29368, U.S. Pat. No. 4,752,597; U.S. Pat. No. 4,808,561; and U.S. Pat. 4,937,299 the teachings of which are incorporated herein by reference. Blends of plastomers can be used. As is known in the art, plastomers can be produced by solution, slurry and gas phase accesses but the preferred materials are produced by metallocene catalysis using a high pressure process by polymerizing ethylene in combination with other olefin monomers, such as butene-1, hexene-1, octene-1 and 4-methyl-1-pentene in the presence of catalyst system comprising a cyclopentadienyl-transition metal compound and an alumoxane.

Plastomers found especially useful in the invention are those sold by Exxon Chemical under the trademark "EXACT" and include linear ethylene-butene copolymers such as EXACT 3024 having a density of about 0.905 g/cc (ASTM D-1505) and a melt index of about 4.5 g/10 min. (ASTM D-2839); EXACT 3025 having a density of about 0.910 g/cc (ASTM D-1505) and a melt index of about 1.2 g/10 min. (ASTM D-2839); EXACT 3027 having a density of about 0.900 g/cc (ASTM D-1505) and a melt index of about 3.5 g/10 min. (ASTM D-2839). Other useful plastomers include but are not limited to ethylene-hexene copolymers such as EXACT 3031 having a density of about 0.900 g/cc (ASTM D-1505) and a melt index of about 3.5 g/10 min. (ASTM D-2839), as well as EXACT 4049, which is an ethylene-butene copolymer having a density of about 0.873 g/cc (ASTM D-1505) and a melt index of about 4.5 g/10 min. (ASTM D-2839). All of the above EXACT series plastomers are available from EXXON Chemical Co.

EXACT plastomers typically have a dispersion index (M_w/M_n , where M_w is weight average molecular weight and M_n is number average molecular weight) of about 1.5 to 4.0, preferably 1.5–2.4, a molecular weight of about 5,000 to 50,000, preferably about 20,000 to about 30,000 a density of about 0.86 to about 0.93 g/cc, preferably about 0.87 g/cc to about 0.91 g/cc, a melting point of about 140–220 F, and a melt flow index (MI) above about 0.5 g/10 mins, preferably about 1–10 g/10 mins as determined by ASTM D-1238, condition E. Plastomers which may be employed in the invention include copolymers of ethylene and at least one C_3 – C_{20} -olefin, preferably a C_4 – C_8 -olefin present in an amount of about 5 to about 32 wt %, preferably about 7 to about 22 wt %, more preferably about 9–18 wt %. These plastomers are believed to have a composition distribution breadth index of about 45% or more.

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Plastomers such as those sold by Dow Chemical Co. under the trade name ENGAGE also may be employed in the invention. These plastomers are believed to be produced in accordance with U.S. Pat. No. 5,272,236, the teachings of which are incorporated herein by reference. These plastomers are substantially linear polymers having a density of about 0.85 g/cc to about 0.93 g/cc measured in accordance with ASTM D-792, a melt index (MI) of less than 30 g/10 minutes, a melt flow ratio (I_{10}/I_2) of about 7 to about 20, where I_{10} is measured in accordance with ASTM D-1238 (190/10) and I_2 is measured in accordance with ASTM D-1238 (190/2.16), and a dispersion index M_w/M_n which preferably is less than 5, and more preferably is less than about 3.5 and most preferably is from about 1.5 to about 2.5. These plastomers include homopolymers of C_2 - C_{20} olefins such as ethylene, propylene, 4-methyl-1-pentene, and the like, or they can be interpolymers of ethylene with at least one C_3 - C_{20} -olefin and/or C_2 - C_{20} acetylenically unsaturated monomer and/or C_4 - C_{18} diolefins. These plastomers have a polymer backbone that is either unsubstituted or substituted with up to 3 long chain branches/1000 carbons. As used herein, long chain branching means a chain length of at least about 6 carbons, above which the length cannot be distinguished using ^{13}C nuclear magnetic resonance spectroscopy. The preferred ENGAGE plastomers are characterized by a saturated ethylene-octene backbone and a narrow dispersion index M_w/M_n of about 2. Other commercially available plastomers may be useful in the invention, including those manufactured by Mitsui.

The dispersion index M_w/M_n of plastomers made in accordance with U.S. Pat. No. 5,272,236 most preferably is about 2.0. Non-limiting examples of these plastomers include ENGAGE CL 8001 having a density of about 0.868 g/cc, a melt index of about 0.5 g/10 mins, and a Shore A hardness of about 75; ENGAGE CL 8002 having a density of about 0.87 g/cc, a melt index of about 1 gms/10 min, Shore A hardness of about 75; ENGAGE CL 8003 having a density of about 0.885 g/cc, melt index of about 1.0 gms/10 min, and a Shore A hardness of about 86; ENGAGE EG 8100 having a density of about 0.87 g/cc, a melt index of about 1 gms/10 min., and a Shore A hardness of about 87; ENGAGE 8150 having a density of about 0.868 g/cc, a melt index of about 0.5 gms/10 min, and a Shore A hardness of about 75; ENGAGE 8200 having a density of about 0.87 g/cc, a melt index of about 5 g/10 min., and a Shore A hardness of about 75; and ENGAGE EP 8500 having a density of about 0.87 gms/cc, a melt index of about 5 g/10 min., and a Shore A hardness of about 75.

Fillers

Fillers preferably are used to adjust the density, flex modulus, mold release, and/or melt flow index of the inner cover layer. More preferably, at least when the filler is for adjustment of density or flex modulus, it is present in an amount of at least five parts by weight based upon 100 parts by weight of the resin composition. With some fillers, up to about 200 parts by weight probably can be used. A density adjusting filler according to the invention preferably is a filler which has a specific gravity which is at least 0.05 and more preferably at least 0.1 higher or lower than the specific gravity of the resin composition. Particularly preferred density adjusting fillers have specific gravities which are higher than the specific gravity of the resin composition by 0.2 or more, even more preferably by 2.0 or more. A flex modulus adjusting filler according to the invention is a filler which, when used in an amount of e.g. 1-100 parts by weight based upon 100 parts by weight of resin composition, will raise or

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lower the flex modulus (ASTM D-790) of the resin composition by at least 1% and preferably at least 5% as compared to the flex modulus of the resin composition without the inclusion of the flex modulus adjusting filler. A mold release adjusting filler is a filler which allows for easier removal of part from mold, and eliminates or reduces the need for external release agents which otherwise could be applied to the mold. A mold release adjusting filler typically is used in an amount of up to about 2 wt % based upon the total weight of the inner cover layer. A melt flow index adjusting filler is a filler which increases or decreases the melt flow, or ease of processing of the composition.

The cover layers may contain coupling agents that increase adhesion of materials within a particular layer e.g. to couple a filler to a resin composition, or between adjacent layers. Non-limiting examples of coupling agents include titanates, zirconates and silanes. Coupling agents typically are used in amounts of 0.1-2 wt % based upon the total weight of the composition in which the coupling agent is included.

A density adjusting filler is used to control the moment of inertia, and thus the initial spin rate of the ball and spin decay. The additional a filler with a lower specific gravity than the resin composition results in a decrease in moment of inertia and a higher initial spin rate than would result if no filler were used. The addition of a filler with a higher specific gravity than the resin composition results in an increase in moment of inertia and a lower initial spin rate. High specific gravity fillers are preferred as less volume is used to achieve the desired inner cover total weight. Non-reinforcing fillers are also preferred as they have minimal effect on COR. Preferably, the filler does not chemically react with the resin composition to a substantial degree, although some reaction may occur when, for example, zinc oxide is used in a cover layer which contains some ionomer.

The density-increasing fillers for use in the invention preferably have a specific gravity in the range of 1.0-20. The density-reducing fillers for use in the invention preferably have a specific gravity of 0.06-1.4, and more preferably 0.06-0.90. The flex modulus increasing fillers have a reinforcing or stiffening effect due to their morphology, their interaction with the resin, or their inherent physical properties. The flex modulus reducing fillers have an opposite effect due to their relatively flexible properties compared to the matrix resin. The melt flow index increasing fillers have a flow enhancing effect due to their relatively high melt flow versus the matrix. The melt flow index decreasing fillers have an opposite effect due to their relatively low melt flow index versus the matrix.

Fillers may be or are typically in a finely divided form, for example, in a size generally less than about 20 mesh, preferably less than about 100 mesh U.S. standard size, except for fibers and flock, which are generally elongated. Flock and fiber sizes should be small enough to facilitate processing. Filler particle size will depend upon desired effect, cost, ease of addition, and dusting considerations. The filler preferably is selected from the group consisting of precipitated hydrated silica, clay, talc, asbestos, glass fibers, aramid fibers, mica, calcium metasilicate, barium sulfate, zinc sulfide, lithopone, silicates, silicon carbide, diatomaceous earth, polyvinyl chloride, carbonates, metals, metal alloys, tungsten carbide, metal oxides, metal stearates, particulate carbonaceous materials, micro balloons, and combinations thereof. Non-limiting examples of suitable fillers, their densities, and their preferred uses are as follows in Table 10:

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TABLE 10

	Spec. Grav	Comments
<u>Filler Type</u>		
Precipitated hydrated silica	2.0	1, 2
Clay	2.62	1, 2
Talc	2.85	1, 2
Asbestos	2.5	1, 2
Glass fibers	2.55	1, 2
Aramid fibers (KEVLAR®)	1.441	1, 2
Mica	2.8	1, 2
Calcium metasilicate	2.9	1, 2
Barium sulfate	4.6	1, 2
Zinc sulfide	4.1	1, 2
Lithopone	4.2-4.3	1, 2
Silicates	2.1	1, 2
Silicon carbide platelets	3.18	1, 2
Silicon carbide whiskers	3.2	1, 2
Tungsten carbide	15.6	1
Diatomaceous earth	2.3	1, 2
Polyvinyl chloride	1.41	1, 2
<u>Carbonates</u>		
Calcium carbonate	2.71	1, 2
Magnesium carbonate	2.20	1, 2
<u>Metals and Alloys (powders)</u>		
Titanium	4.51	1
Tungsten	19.35	1
Aluminum	2.70	1
Bismuth	9.78	1
Nickel	8.90	1
Molybdenum	10.2	1
Iron	7.86	1
Steel	7.8-7.9	1
Lead	11.4	1, 2
Copper	8.94	1
Brass	8.2-8.4	1
Boron	2.34	1
Boron carbide whiskers	2.52	1, 2
Bronze	8.70-8.74	1
Cobalt	8.92	1
Beryllium	1.84	1
Zinc	7.14	1
Tin	7.31	1
<u>Metal Oxides</u>		
Zinc oxide	5.57	1, 2
Iron oxide	5.1	1, 2
Aluminum oxide	4.0	1, 2
Titanium oxide	3.9-4.1	1, 2
Magnesium oxide	3.3-3.5	1, 2
Zirconium oxide	5.73	1, 2
<u>Metal Stearates</u>		
Zinc stearate	1.09	3, 4
Calcium stearate	1.03	3, 4
Barium stearate	1.23	3, 4
Lithium stearate	1.01	3, 4
Magnesium stearate	1.03	3, 4
<u>Particulate carbonaceous materials</u>		
Graphite	1.5-1.8	1, 2
Carbon black	1.8	1, 2
Natural bitumen	1.2-1.4	1, 2
Cotton flock	1.3-1.4	1, 2
Cellulose flock	1.15-1.5	1, 2
Leather fiber	1.2-1.4	1, 2
<u>Micro balloons</u>		
Glass	0.15-1.1	1, 2
Ceramic	0.2-0.7	1, 2

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TABLE 10-continued

	Spec. Grav	Comments
5 Fly ash	0.6-0.8	1, 2
Coupling Agents Adhesion Promoters		
Titanates	0.95-1.17	
Zirconates	0.95-1.11	
10 Silane	0.95-1.2	

- 1 Particularly useful for adjusting density of the inner cover layer.
 2 Particularly useful for adjusting flex modulus of the inner cover layer.
 3 Particularly useful for adjusting mold release of the inner cover layer.
 4 Particularly useful for increasing melt flow index of the inner cover layer.

15 All fillers except for metal stearates would be expected to reduce the melt flow index of the inner cover layer.

The amount of filler employed is primarily a function of weight requirements and distribution.

20 Ionomeric Resins

Ionomeric resins include copolymers formed from the reaction of an olefin having 2 to 8 carbon atoms and an acid which includes at least one member selected from the group consisting of alpha, beta-ethylenically unsaturated mono- or dicarboxylic acids with a portion of the acid groups being neutralized with cations. Terpolymer ionomers further include an unsaturated monomer of the acrylate ester class having from 1 to 21 carbon atoms. The olefin preferably is an alpha olefin and more preferably is ethylene. The acid preferably is acrylic acid or methacrylic acid. The ionomers typically have a degree of neutralization of the acid groups in the range of about 10-100%.

35 The present invention is further illustrated by the following examples in which the parts of the specific ingredients are by weight. It is to be understood that the present invention is not limited to the examples, and various changes and modifications may be made in the invention without departing from the spirit and scope thereof.

40 EXAMPLE 1

Cores and Related Properties

Using the ingredients tabled below, golf ball cores having a finished diameter of about 1.470 to about 1.475 inches were produced by compression molding and subsequent removal of a surface layer by grinding. Each core was formulated using 100 parts elastomer (rubber). In the formulations, the amounts of remaining ingredients are expressed in parts by weight, and the coefficient of restitution and compression achieved are set forth below.

Tables 11 and 12 summarize the results of testing of four core compositions.

TABLE 11

Composition of Golf Ball Cores

Component	Trial			
	1 Control	2	3	4
Cariflex BR-1220 ²	100	—	—	—
Cariflex BCP-820 ¹	—	100	40	40
Neo Cis 60 ³	—	—	60	—
CB-22 ⁴	—	—	—	60
65 Zinc Oxide (activator filler)	30.9	31	30.7	30.2
Zinc Stearate (activator)	16	16	16	16

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TABLE 11-continued

Composition of Golf Ball Cores				
Component	Trial			
	1 Control	2	3	4
ZDA (zinc diacrylate)	21.1	20.9	21.5	22.5
231 XL (peroxide)	0.90	0.90	0.90	0.90
	168.9	168.8	169.1	169.6

¹See Table 1 for a description and properties of Cariflex BCP-B20²See Table 4 for a description and properties of Cariflex BR-1220³See Table 2 for a description and properties of Neo Cis 60⁴See Table 3A for a description and properties of Buna CB-22

TABLE 12

Properties of Golf Ball Cores				
Property	Trial			
	1 Control	2	3	4
Size (pole dia. inches)	1.474	1.474	1.473	1.475
Weight (grams)	33.3	33.3	33.2	33.3
Riehle Compression	0.112	0.109	0.112	0.113
C.O.R.	0.776	0.785	0.781	0.781
Nes Factor ¹	.888	.894(+6)	.893(+5)	.894(+6)

¹Nes Factor is the sum of the C.O.R. and the Riehle compression. The higher the number the higher the resilience. This adjusts the results for compression, i.e. Trial #2 has a compression of 0.109, this is 3 points harder than the control and is 9 points faster in C.O.R. than the control. This is a net gain of 6 points. Trial #3 has exactly the same compression as the control and needs no Nes Factor correction as both the C.O.R. and Nes Factor are 5 points higher.

The results of Table 12 show that the high Mooney BCP-820 is 9 points higher in C.O.R. vs. the control (low Mooney BR-1220). Blends of the high Mooney BCP-820 with Neodymium catalyzed Neo Cis 60 and CB-22 also show a 5 to 6 point gain in C.O.R.

The high Mooney BCP-820, while giving high C.O.R. values, is extremely difficult to process using conventional equipment. Blending the high Mooney BCP-820 with Neodymium catalyzed polybutadiene rubber solves the processing problems but maintains the high C.O.R. values.

Tables 13 and 14 summarize the results of additional testing.

TABLE 13

Composition of Golf Ball Cores						
Component	Trial					
	1	2	3	4	5	6
Cariflex BCP-B20	100	—	—	40	40	20
Neo Cis 40	—	100	—	60	—	—
Neo Cis 60	—	—	100	—	60	80
Zinc Oxide	31	31	31	31	31	31
Zinc Stearate	16	16	16	16	16	16
ZDA	20.9	20.9	20.9	20.9	20.9	20.9
231 XL	0.90	0.90	0.90	0.90	0.90	0.90
	168.8	168.8	168.8	168.8	168.8	168.8

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TABLE 14

Properties of Golf Ball Cores						
Property	Trial					
	1	2	3	4	5	6
Size (pole dia. inches)	1.476	1.475	1.476	1.476	1.476	1.476
Weight (grams)	33.4	33.3	33.4	33.4	33.4	33.3
Riehle Compression	0.107	0.119	0.116	0.115	0.112	0.114
C.O.R.	0.785	0.773	0.777	0.776	0.780	0.778
Nes Factor	.892	.892	.893	.891	.892	.892

The results in Table 14 show there is very little difference in the 6 trials when the C.O.R. is corrected for differences in compression, i.e. Nes Factor. The Neodymium rubber when used at 100% or when blended with high Mooney BCP-820 is equal to the properties of the high Mooney BCP-820 when used at 100%. Neodymium rubber when used at 100% is also extremely difficult to process due to high die swell during extrusion of preforms and high cold flow of the rubber causing deformed preforms resulting in very high rejects. Neodymium polybutadiene and high Mooney polybutadiene rubber such as BCP 820 cannot be processed when used alone at 100 parts or conventional equipment such as two roll mills and extruders.

When the two rubbers above are blended together, processing of the synergistic mixture becomes easy and practical without losing any performance or C.O.R.

Tables 15 and 16 summarize the results of testing of four additional core compositions.

TABLE 15

Composition of Golf Ball Cores				
Component	Trial			
	1	2	3	4
Cariflex BR-1220 ¹	70	100	—	—
Taktene 220 ²	30	—	—	30
Shell BCP 820 ³	—	—	100	70
ZnO (activator filler)	31.5	31.5	31.5	31.5
Regrind (ground flash)	16	16	16	16
Zn Stearate (activator)	16	16	16	16
ZDA (zinc diacrylate)	21.5	21.5	21.5	21.5
231 XL (peroxide)	0.90	0.90	0.90	0.90
Total	185.9	185.9	185.9	185.9

¹See Table 4 for properties of Cariflex BR-1220²See Table 5A and 5B for properties of Taktene 220³See Table 1 for properties of Shell BCP-820

TABLE 16

Properties of Golf Ball Cores				
Property	Trial			
	1 Control	2	3	4
Size (dia. inches)	1.493	1.492	1.492	1.492
Weight (grams)	34.4	34.4	34.5	34.4
Riehle Compression	.099	.095	.093	.096
C.O.R.	0.778	0.781	0.787	0.782
Durability	Pass	Pass	Pass	Pass
Nes Factor ¹	.877	.876	.880	.878

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TABLE 16-continued

Property	Properties of Golf Ball Cores			
	Trial			
	1	2	3	4
	Control			

¹Nes Factor is the sum of the C.O.R. and Riehle compression. The higher the number the higher the resilience. This adjusts the results for compression, i.e. Trial #3 is 6 points harder than the control but is 9 points faster in C.O.R. This is a net gain of 3 points. (If the ZDA level is adjusted in each trial so that the compression is exactly the same, then trial #3 would be 3 points higher in C.O.R.)

Tables 17 and 18 summarize the results of testing of additional core compositions.

TABLE 17

Component	Composition of Golf Ball Cores	
	Trial	
	1	2
	Control	
Cariflex BR-1220	70	—
Taktene 220	30	—
Shell BCP-820	—	100
ZnO	31.5	32.0
Regrind	16	16
Zn Stearate	16	16
ZDA	21.5	20.5
231XL	0.90	0.90
Total	185.9	185.4

TABLE 18

Property	Properties of Golf Ball Cores	
	Trial	
	1	2
	Control	
Size (dia. inches)	1.542	1.543
Weight (grams)	37.8	38.0
Riehle Compression	.093	.093
C.O.R.	0.775	0.782
Nes factor	.868	.875

Tables 17 and 18 demonstrate that when the Zinc Diacrylate (ZDA) level is adjusted to obtain the same Riehle compression as the Control, the C.O.R. increased 7 points higher for the BCP-820 and the Nes Factor was also 7 points higher.

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Tables 19 and 20 summarize the results of additional testing of core compositions.

TABLE 19

Component	Composition of Golf Ball Cores		
	Trial		
	1	2	3
	Control		
Cariflex BR-1220	70	100	—
Taktene 220	30	—	—
Shell BCP-820	—	—	100
ZnO	31.5	31.7	31.8
Regrind	16	16	16
Zn Stearate	16	16	16
ZDA	21.5	21.1	19.9
231 XL	0.90	0.90	0.90
Total	185.9	185.7	184.6

TABLE 20

Property	Properties of Golf Ball Cores		
	Trial		
	1	2	3
	Control		
Size (dia. inches)	1.493	1.493	1.494
Weight (grams)	34.5	34.4	34.3
Riehle Compression	.098	.104	.106
C.O.R.	0.777	0.773	0.776
Nes Factor	.875	.877	.882

Tables 19 and 20 demonstrate that, despite adjusting the ZDA level, the Riehle compressions were different. However, the Nes Factor shows that Trial #3 using 100% BCP-820 is 7 points higher than the Control.

Table 21 summarizes additional testing.

TABLE 21

Component	Composition of Golf Ball Cores	
	Trial	
	1	2
	Control	
Cariflex BR-1220	70	—
Taktene 220	30	—
BCP-820	—	100
ZnO	31.5	31.8
Regrind	16	16
Zn Stearate	16	16
ZDA	20	19.4
231 XL	0.90	0.90
TOTAL	184.4	184.1

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Tables 22A-22D and 23 summarize the resulting balls and their components.

TABLE 22A

Properties of Cores, Mantled Cores, Molded and Finished Balls		
Core Property	Trial	
	1	2
	Control	
Size (dia. inches)	1.508	1.511
Weight (grams)	35.4	35.7
Riehle Compression	.105	.98
C.O.R.	0.771	0.781
Nes Factor	.876	.879 (+3)

Cores were centerless ground to 1.470" and injection molded with a high modulus clear ionomer mantle. See Table 23 for mantle composition.

TABLE 22B

Mantled Cores	1	2
	Control	
Size (dia. inches)	1.568	1.570
Weight (grams)	38.4	38.4
Riehle Compression	.085	.081
C.O.R.	0.802	0.808
Nes Factor	.887	.889 (+2)

Mantled cores were injection molded with a soft, low modulus ionomer cover into dimpled molded golf balls. See Table 23 for cover composition.

TABLE 22C

Molded Golf Balls	1	2
	Control	
Size (dia. inches)	1.683	1.683
Weight (grams)	45.3	45.4
Riehle Compression	.081	.080
C.O.R.	0.787	0.792
Nes Factor	.868	.872 (+4)

Molded balls were trimmed, brush tumbled, primed, stamped, and clear coated.

TABLE 22D

Finished Golf Balls	1	2
	Control	
Size (dia. inches)	1.682	1.682
Weight (grams)	45.6	45.7
Riehle Compression	.080	.080
C.O.R.	0.786	0.790
Nes Factor	.866	.870 (+4)

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TABLE 23

Composition of Mantle and Cover	
Mantle Component	
Iotek 1002/S031	50
Iotek 1003/S041	50
	100
Cover Component	
Iotek 7510	41
Iotek 7520	41
Iotek 8000	8.5
T.G. White M.B.	9.4
	99.9

It is evident from the proceeding tables that the high Mooney cobalt catalyzed polybutadiene BCP-820 produces a higher C.O.R. (3-7 points) vs. the low Mooney cobalt catalyzed polybutadiene. Blending with the low Mooney polybutadiene produces less of a gain in C.O.R.

EXAMPLE 2

Manufacture of Golf Balls

A number of golf ball cores were made having the following formulation and characteristics as shown in Table 24.

TABLE 24

Material	Weight
High Cis Polybutadiene Cariflex BR-1220 ¹	70
High Cis polybutadiene Taktene 220 ²	30
Zinc Oxide ³	25
Core Regrind ⁴	20
Zinc Stearate ⁵	15
Zinc Diacrylate ⁶	18
Red Colorant	.14
Peroxide (Luperco 23/XL or Triganox 29/40) ⁷	.90

¹Muehlstein, Norwalk, CT

²Bayer Corp., Akron, OH

³Zinc Corp of America, Monaca, PA

⁴golf ball core regrind (internal source)

⁵Synpro, Cleveland, OH

⁶Rockland React Rite, Rockland, GA

⁷R.T. Vanderbilt, Norwalk, CT

The cores had a diameter of 1.560 inches, a PGA compression of about 40 and a COR of about 0.775. To make the cores, the core ingredients were intimately mixed in an internal mixer until the compositions were uniform, usually over a period of from about 5 to about 20 minutes. The sequence of addition of the components was not found to be critical. As a result of shear during mixing, the temperature of the core mixtures rose to about 190° F. whereupon the batch was discharged onto a two roll mill, mixed for about one minute and sheeted out.

The sheet was rolled into a "pig" and then placed in a Barwell preformer and slugs produced. The slugs were then subjected to compression molding at about 310° F. for about 11½ minutes. After molding, the cores were cooled under ambient conditions for about 4 hours. The molded cores were then subjected to a centerless grinding operation whereby a thin layer of the molded core was removed to produce a round core having a diameter of 1.2 to 1.5 inches. Upon completion, the cores were measured for size and in some instances weighed and tested to determine compression and COR.

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The cores were covered with an injection-molded cover blend of 35 parts by weight EX® 1006 (Exxon Chemical Corp., Houston, Tex.), 55.6 parts by weight EX 1007 (Exxon Chemical Corp., Houston, Tex.) and 9.4 parts by weight of Masterbatch. The Masterbatch contained 100 parts by weight Iotek 7030, 31.72 parts by weight titanium dioxide (Unitane 0-110), 0.6 parts by weight pigment (Ultramarine Blue), 0.35 parts by weight optical brightener (Eastobrite OB1) and 0.05 parts by weight stabilizer (Santanox R).

The cover had a thickness of 0.055 inches and a Shore D hardness of 67. The balls had a PGA compression of 65 and a COR of 0.795.

EXAMPLE 3

Manufacture of Golf Balls

The procedure of Example 2 was repeated with the exception that a different cover formulation was used.

The cores were covered with a cover blend of 54.5 parts by weight Surlyn 9910, 22.0 parts by weight Surlyn 8940, 10.0 parts by weight Surlyn 8320, 4.0 parts by weight Surlyn 8120, and 9.5 parts by weight of Masterbatch. The Masterbatch had the same formulation as that of Example 2.

The cover had a thickness of 0.55 inches and a Shore D hardness of 63. The balls had a PGA compression of 63 and a COR of 0.792.

EXAMPLE 4

Frequency Measurements of Golf Club/Ball Contact Based Upon Sound

A number of frequency measurements based upon audible sound were made for the sound of contact between a putter and 11 different types of golf balls, including the balls of Example 2. Three balls of each type were tested.

The putter was a 1997 Titleist Scotty Cameron putter. An accelerometer (Vibra-Metrics, Inc., Hamden, Conn., Model 9001A, Serial No. 1225) was placed on the back cavity of the putter head. The output of the accelerometer was powered by a Vibra-Metrics, Inc., Hamden, Conn., Model P5000 accelerometer power supply, at a gain of x1. A microphone was positioned proximate to the intended point of contact between the putter and the ball. The microphone stand was placed at the distal end of the putter head such that the microphone itself was positioned 3 centimeters above the sweet spot at a downfacing angle of 30°. A preamplifier (Realistic Model 42-2101A, Radio Shack) was used for the microphone. Signals were collected using a Metrabyte DAS-58 A-D board with a SSH-04 simultaneous sample and hold module (Keithley Instruments, Cleveland, Ohio) at a rate of 128 kHz. The microphone was a Radio Shack Model 33-3007 unidirectional condenser microphone with a frequency response of 50-15000 Hz.

The putter was positioned by a putting pendulum so that when properly balanced the ground clearance was one millimeter. The balls were hit from the sweet spot of the putter. The club was drawn back to the 20° mark on the putting pendulum. Contact with the ball occurred when the putter was at a 90° angle relative to the ground.

The point of contact between the club and the ball could be determined by viewing the signal from the accelerometer. Pre-trigger and post-trigger data was collected for each shot. Data was collected at 128 kHz for a duration of 64 microseconds, resulting in 8,192 data points per shot. The data was saved in ASCII text files for subsequent analysis.

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Each ball was struck 10 times in a random sequence, i.e., all 33 balls were struck before any ball was struck a second time and the striking order was randomly changed for each set of hits. Data for the three balls of each particular type was averaged. The results are shown below on Table 25.

TABLE 25

MANU.	BALL	SOUND FREQ.	STD. DEV.	COR (x1000)	PGA COMP
Top Flite	Example 2	3.12	0.06	800	67
	Strata Tour 90	3.20	0.18	772	92
	Strata Tour 100	3.46	0.03		
	Tour Balata (W)	3.31	0.18	780	78
	HP2 Tour	3.73	0.29	772	92
Titleist	DT Wound 100	3.66	0.29		
	DT 2P (90)	3.39	0.04	820	99
	HP2 Dist (90)	3.33	0.14	803	99
	Professional 100	3.70	0.30	780	93
Maxfli	XF 100	4.45	0.27	780	90
Bridgestone	Precept DW	3.40	0.08	785	93

As shown by the results on Table 25, the balls of Example 2 had a lower frequency measurement based upon sound than all of the other balls that were tested.

EXAMPLE 5

Golf Ball Mechanical Impedance and Natural Frequency Determinations

Mechanical impedance and natural frequency of the golf balls of the invention were determined, along with the mechanical impedance and natural frequency of commercially available golf balls.

Impedance was determined using a measurement of acceleration response over sine-sweep based frequencies.

FIG. 13 schematically shows the equipment used to determine mechanical impedance of golf balls in accordance with the present invention. A power amplifier 210 (IMV Corp. PET-0A) was obtained and connected to a vibrator 212 (IMV Corp. PET-01). A dynamic signal analyzer 214 (Hewlett Packard 35670A) was obtained and connected to the amplifier 210 to provide a sine-sweep source to 10,000 Hz. An input accelerometer 216 (PCB Piezotronics, Inc., New York, A353B17) was physically connected to the vibrator 212 (with Loctite 409 adhesive and electrically connected to the dynamic signal analyzer 214. The dynamic signal analyzer 214 was programmed such that it could calculate the mechanical impedance given two acceleration measurements and could plot this data over a frequency range.

An output accelerometer 218 (PCB Piezotronics, Inc., New York, A353B17) was obtained and electrically connected to the dynamic signal analyzer 214. A first golf ball sample 220 was obtained and bonded to the vibrator 212 using Loctite 409 adhesive. The output accelerometer 218 also was bonded to the ball using Loctite 409 adhesive. The vibrator 212 was turned on and a sweep was made from 100 to 10,000 Hz. Mechanical impedance was then plotted over this frequency range.

The natural frequency was determined by observing the frequency at which a second minimum occurred in the impedance curve. The first minimum value was determined to be a result of forced node resonance resulting from contact with the accelerometer 218 or the vibrator 212. This determination about the first minimum value is based upon separate tests which compared the above described mechanical impedance test method, referred to the "sine-sweep

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method" of determining mechanical impedance, as compared to an "impact method" in which a golf ball is suspended from a string, and is contacted with an impact hammer on one side with accelerometer measurements taken opposite the impact hammer.

The mechanical impedance and natural frequency of the balls of Examples 2 and 3 above were determined using the above-described method. The first set of data was taken with the balls at room temperature. The second set of data was taken after the balls had been maintained at 21.1° C. (70° F.) for a period of time, preferably at least 15 hours. Furthermore, 12 commercially available golf balls also were tested. The results are shown below on Table 26.

TABLE 26

BALL	NAT. FREQ. (Hz)	NAT. FREQ. (Hz)	COR	PGA COMP
Example 2	3070 Hz	2773	799	67
Example 3	2773 Hz	2575	792	63
Top-Flite				
Strata Tour 90	3268 Hz	2674	772	92
Magna Ex	3268 Hz	3169		
Z Balata 90		3268		
Titleist				
Tour Balata 100 (wound)	3070	2773	780	78
Professional 100 (wound)	3862 Hz		780	93
DT Wound 100 (wound)	3664 Hz	2872		
HP2 Tour	3763 Hz		772	92
Tour Balata 90 (wound)		2674		
Wilson				
Staff Ti Balata 100	3565 Hz		791	90
Staff Ti Balata 90		3466		
Ultra 500 Tour Balata	3862 Hz			100
Bridgestone				
Precept EV Extra Spin	3664 Hz		785	93
Precept Dynawing	3466 Hz		803	87
Maxfli				
XF100	3763 Hz		780	90
RM 100	3466 Hz		792	84
Sumitomo				
Srixon Hi-brid		2773		

Additionally, a non-commercial, non-wound ball with a liquid (salt/sugar water) core was tested and was found to have a natural frequency of 3961.

As shown by the results on Table 26, the balls of the present invention have a low natural frequency in combination with a relatively high COR. The low natural frequency provides the balls with a soft sound and feel while maintaining good distance.

EXAMPLE 6

Measurement of Core Hardness Gradient

Another series of trials were carried out in which the core hardness gradient was measured for the most preferred core composition according to the present invention. As will be recalled, that most preferred core composition is set forth in Table 6 herein.

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TABLE 27

Most Preferred Core Composition (Set Forth in Table 6)	
Surface	76
5 mm in	71
10 mm in	67
15 mm in	65
Center	63
5 mm out	66
10 mm out	68
15 mm out	69
Core Size	1.560"

EXAMPLE 7

Production and Testing of Preferred Embodiment Golf Balls

In yet another series of trials, a series of particularly preferred cores and covers were formed to produce particularly preferred golf balls in accordance with the present invention. These preferred cover compositions and core compositions are set forth below in Tables 28A and 28B, respectively.

TABLE 28

Cover Compositions					
Materials	39A (wt %)	39B (wt %)	39C (wt %)	39D (wt %)	39E (wt %)
Iotek 1006	—	43.75	—	—	43.75
Iotek 1007	—	43.75	—	—	—
Suriyn 8940	21	—	—	—	—
Suriyn 9910	52.8	—	—	—	—
Suriyn 8120	4	—	—	—	—
Suriyn 8320	9.7	—	—	—	—
Suriyn 8140	—	—	35	—	—
Suriyn 6120	—	—	52.5	87.5	43.75
Shite MB	12.5	12.5	12.5	12.5	12.5

TABLE 28B

Core Formulations			
Materials	37A (pph)	37B (pph)	37C (pph)
BCP-820	45	45	45
Neo Cis 40	55	55	55
Zinc Oxide	29.5	23.9	23.2
Zinc Stearate	16	16	16
Zinc Diacrylate (ZDA)	18.4	20.4	21.9
Lavender MB	—	0.14	—
Blue MB	—	—	—
Yellow MB	0.14	—	0.14
Triganox 42-40B	1.25	1.25	1.25

Golf balls were produced using various combinations of these cover and core compositions. A summary of these balls is set forth below in Table 28C. The noted barrel test is utilized to determine an indication of durability. This test is described in detail in U.S. Pat. Nos. 5,827,134 and 5,820,489 herein incorporated by reference. Basically, the test involves the use of an air cannon that fires a golf ball at about 135 ft/second into a five-sided steel drum until the ball breaks. One dozen of each ball type is tested. The average is the average number of runs until the ball breaks. Higher averages indicate greater durability.

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TABLE 28C

Sample	1 37A	2 37A	3 37A	4 37B	5 37B	6 37B	7 37B	8 37B	9 37C	10 37C	11 37C
<u>CORE</u>											
Size	1.500"	1.500"	1.500"	1.560"	1.560"	1.560"	1.560"	1.560"	1.560"	1.560"	1.560"
Weight	34.3	34.3	34.3	37.8	37.8	37.8	37.8	37.8	37.8	37.8	37.8
Comp	134	134	134	116	116	116	116	116	106	106	106
COR	766	766	765	781	781	781	781	781	786	786	786
<u>COVER</u>											
39A				X							
39B	X				X				X		
39C		X				X				X	
39D			X				X				X
39E								X			
<u>FINISHED</u>											
Cover Thickness	0.090"	0.090"	0.09"	0.060"	0.060"	0.060"	0.060"	0.060"	0.060"	0.060"	0.060"
Size	1.68	1.681	1.682	1.683	1.683	1.684	1.685	1.683	1.683	1.684	1.685
Weight	45.3	45.3	45.3	45.5	45.4	45.5	45.5	45.4	45.4	45.5	45.5
Riehle Comp	90	82	87	97	94	89	91	91	88	83	85
COR	809	815	807	803	812	816	812	814	814	818	814
Shore D	67	70-71	69-70	65	67	70-71	69-70	69	67	70-71	69-70
Cold Crack	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
Barrel (1 dozen)											
Durability											
Avg	309	283	325	312	285	269	315	308	348	306	375
Min	256	206	256	272	225	206	194	239	256	225	281
max	500	332	380	380	344	306	541	380	500	352	570
# above 300	7	3 (of 13)	10	7	3	1 (of 11)	5	6	10	7	11

All core formulations are in accordance with the present invention. Sample 4 may be considered a control. All other balls utilized a harder cover. This reduced spin and resulted in superior COR.

In another set of trials, a series of particularly preferred cores and covers were formed to produce particularly preferred golf balls in accordance with the present invention. These preferred cover compositions and core compositions are set forth below in Tables 29A and 29B, respectively.

TABLE 29A

Materials	Cover A (wt %)	Cover B (wt %)	Cover C (wt %)
Iotek 1006	—	35	—
Iotek 1007	—	52.5	—
Surllyn 8140	35	—	—
Surllyn 6120/8552	52.5	—	—
Surllyn 9910	—	—	54.6
Surllyn 8940	—	—	22
Surllyn 8120	—	—	4
Surllyn 8320	—	—	10
White MB	12.5	12.5	9.4

TABLE 29B

	<u>Control</u>		
	1	2	3
Cariflex BR-1220	70		
Taktene 1220	30		
BCP-820		40	40
Nes Cis 60		30	30
Nes Cis 40		30	30
ZnO	24.9	23.2	23.7
T.G. Re grind	20		
Zn Stearate	15	16	16
Zinc Diacrylate (ZDA)	18.3	21.7	20.7
Color M.B.	.14		.14
231 XL	Red 0.90	White 1.25	Lav. 1.25
size pole	179.24	162.15	161.79
wgt.	1.560	1.557	1.557
Comp.	37.8	37.6	37.6
COR	114	109	114
	.775	.789	.787

These various preferred cover and core formulations were utilized to provide a series of particularly preferred golf balls. A summary of these balls is set forth in Table 29C.

TABLE 29C

Sample	1	2	3	4	5	6	7	8	9
<u>Core Data</u>									
Nos.	1(C)	2	3	1(C)	2	3	1(C)	2	3
Size	1.56	1.557	1.557	1.56	1.557	1.557	1.56	1.557	1.557

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TABLE 29C-continued

Sample	1	2	3	4	5	6	7	8	9
Weight	37.8	37.6	37.6	37.8	37.6	36.6	37.8	37.6	37.6
Comp	114	109	114	114	109	114	114	109	114
COR	775	789	787	775	789	787	775	789	787
Cover Type									
Magna Ex (C)							X	X	X
1006/1007 (B)					X	X	X		
814016120 (A)	X	X	X						
Ball Data									
PGA Comp.	69	74	70	65	70	65	63	66	63
Riehl Comp	91	86	90	95	90	95	97	94	97
COR	810	820	818	803	813	812	796	806	804
Shore D	70	70	70	67	67	67	64	64	64
Barrel (Avg)		503			615			660	
Durability									
Min		302			456			433	
Max		696			818			852	
NES Factor	901	906	908	898	903	907	893	900	901

Sample 7 may be considered a control. The cores used in Samples 1, 4 and 7 are controls.

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EXAMPLE 8

An additional embodiment according to the present invention utilizes blends of the Neo Cis polymers in the core compositions. The following Table represents core formulations which utilizes a blend of Neo Cis 40 and Neo Cis 60 with Cariflex BCP-820 (amounts of ingredients are in parts per hundred rubber (phr) based on 100 parts butadiene rubber):

TABLE 30

	Formulation No.			
Ingredient	1	2	3	4
Cariflex BCP-820	40	40	40	40
Neo Cis 60	30	30	30	30
Neo Cis 40	30	30	30	30
Zinc Oxide	31.4	30.9	26	24.6

TABLE 30-continued

	Formulation No.			
Ingredient	1	2	3	4
Zinc Stearate	16	16	16	16
ZDA	18.2	19.2	18.2	19.6
Yellow MB	0.14	—	—	—
Green MB	0.05	—	—	—
Black MB	—	0.2	—	—
Red MB	—	—	0.075	0.075
Blue MB	—	—	0.075	0.075
Triganox 42-40B	1.25	1.25	1.25	1.25

The core formulations set forth above in Table 30 were then utilized to produce the following corresponding cores:

TABLE 31

	Core Sample			
Property	1	2	3	4
Size (pole dia. inches)	1.47" ± 0.004	1.47" ± 0.004	1.47" ± 0.004	1.47" ± 0.004
Weight (grams)	33.3 g ± 0.3	33.3 g ± 0.3	31.5 ± 0.3	31.5 ± 0.3
Riehl Comp.	134 ± 10	125 ± 10	145 ± 8	135 ± 8
C.O.R.	0.775 ± 0.015	0.765 ± 0.015	0.760 ± 0.015	0.770 ± 0.015
Specific Gravity	1.194 ± 0.005	1.194 ± 0.05	1.168	1.168
JIS C	69 ± 2	71 ± 2	70 ± 2	71 ± 2
Shore C	69 ± 2	71 ± 2	70 ± 2	71 ± 2
Shore D	40 ± 2	42 ± 2	41 ± 2	42 ± 2

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In a preferred embodiment, the cores utilizing the blend of Neo Cis 40 and Neo Cis 60 have a mantle or inner cover layer formed thereon. A variety of ionomers may be utilized in the mantle or inner cover layer of the multi-layer golf balls according to the present invention. Ionomeric resins such as those designated as Surlyn®, manufactured by DuPont, and Iotek, manufactured by Exxon, are suitable for

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forming the mantle layer, but any polymer conventionally used to form inner cover layers in the multi-layer golf balls can be used. The following Table 32 includes ionomers which are exemplary of specific ionomers which may be utilized in the inner cover layer of multi-layer balls according to the present invention. These examples are not intended to be limiting of the specific ionomers which can be used.

TABLE 32

Individual Ionomers			
	Iotek 1002	Iotek 1003	Surlyn® 8552
% Acid Type	18% AA	18% AA	19% MA
Ionomer Type	Copolymer	Copolymer	Copolymer
Cation	Na	Zn	Mg
Melt Index	2	1	1.3
Stiffness Modulus *2	4053 MPa	1873 MPa	3499 Kgf/cm ²

AA = Acrylic Acid; MA = Methacrylic Acid

*2 Stiffness measurements done using Toyoseiki Stiffness Tester

The mantle layer may also contain other additives such as heavy weight fillers including bronze, brass, tungsten, and the like.

The following represents various intermediate golf balls formed from the cores of Table 31.

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TABLE 33

Intermediate Ball with Inner Cover				
	1	2	3	4
Core Formulation (From Table 31)	1	2	3	4
Mantle Composition (Wt %)				
Iotek 1002 (Na)	50%	50%	35%	35%
Iotek 1003 (Zn)	50%	50%	—	—
Surlyn 8552 (Ma)	—	—	65%	65%
Filler (Bronze Powder)	—	—	19.0 pph	19.0 pph
TiO ₂	—	—	0.1 pph	0.1 pph

The inner cover layers, or mantles, as set forth in Table 33 above have the following characteristics as shown in Table 34 below:

TABLE 34

Intermediate Ball (from Table 33)				
Property	1	2	3	4
Flex Modulus (weighted avg.)	264 MPa	264 MPa	264 MPa	264 MPa
Stiffness Modulus	3521 Kgf/cm ²	3521 Kgf/cm ²	3521 Kgf/cm ²	3521 Kgf/cm ²
Size (Intermediate ball)	1.570" ± 0.004	1.570" ± 0.004	1.570" ± 0.004	1.570" ± 0.004
Weight (intermediate ball)	38.3 g ± 0.3	38.3 g ± 0.3	38.3 g ± 0.3	38.3 g ± 0.3
Thickness	0.050" ± 0.008	0.050" ± 0.008	0.050" ± 0.008	0.050" ± 0.008
Rieble comp	122 ± 12	112 ± 12	112 ± 12	106 ± 8
C.O.R.	0.780 ± 0.015	0.790 ± 0.015	0.790 ± 0.015	0.795 ± 0.015
Mantle Specific Gravity	0.96 ± 0.01	0.96 ± 0.01	1.12 ± 0.05	1.12 ± 0.05
IIS C	97 ± 1	97 ± 1	97 ± 1	97 ± 1
Shore C	97 ± 1	97 ± 1	97 ± 1	97 ± 1
Shore D	70 ± 1	70 ± 1	70 ± 1	70 ± 1

The intermediate balls, as shown in Table 33 were then formed into finished golf balls by covering them with an outer cover formulation. The covers are typically ionomeric but other polymers may be utilized in the covers as set forth herein before. Ionomers typically associated with the golf balls according to the present invention include those designated as Surlyn®, manufactured by DuPont, and Iotek, manufactured by Exxon. The ionomers may be used individually or in blends. The following Table 35 includes ionomers which are exemplary of specific ionomers that may be utilized for the outer cover layer of golf balls according to the present invention.

TABLE 35

Outer Cover Ionomers									
	Surlyn 8940	Surlyn 9910	Surlyn 8320	Surlyn 8120	Surlyn 8549	Iotek 7030	Iotek 7510	Iotek 7502	Iotek 8000
% Acid Type	15% MA	15% MA	~7% MA	~7% MA	15% MA	15% AA	6% AA	6% AA	15% AA
Ionomer Type	Copolymer	Copolymer	Terpolymer	Terpolymer	Copolymer	Copolymer	Terpolymer	Terpolymer	Copolymer
Cation	Na	Zn	Na	Na	Na	Zn	Zn	Zn	Na
Melt Index	2.8	0.7	0.8	2	2.3	2.5	0.8	2	2

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TABLE 35-continued

Outer Cover Ionomers									
	Surlyn 8940	Surlyn 9910	Surlyn 8320	Surlyn 8120	Surlyn 8549	Iotek 7030	Iotek 7510	Iotek 7502	Iotek 8000
Stiffness	2705	2874	168	492	—	1840	284	270 MPa	3323
Modulus #2	Kgf/cm ²	Kgf/cm ²	Kgf/cm ²	Kgf/cm ²	—	Kgf/cm ²	Kgf/cm ²	Kgf/cm ²	

AA = Acrylic Acid; MA = Methacrylic Acid

*2 Stiffness measurements done using Toyoseiki Stiffness Tester

The intermediate golf balls of Table 33 were then covered with cover formulations to produce the following finished golf balls:

TABLE 36

Finished Ball	A	B	C	D
Intermediate Ball (from Table 33)	1	2	3	4
Cover Composition (Wt %)				
Surlyn 8549 (Na)	7.3%	7.3%	—	—
Iotek 7510 (Zn)	42%	42%	—	58.9%
Iotek 7520 (Zn)	50.7%	50.7%	—	—
Surlyn 8940 (Na)	—	—	17%	—
Surlyn 9910 (Zn)	—	—	50.1%	—
Surlyn 8320 (Na)	—	—	17.9%	—
Surlyn 8120 (Na)	—	—	7.7%	—
Iotek 7030 (Zn)	—	—	7.3%	7.3%
Iotek 8000 (Na)	—	—	—	33.8%
Whitener (TiO ₂)*	2.3 phr	2.3 phr	2.3 phr	2.3 phr

*Amount based on parts per hundred resin

The finished balls of Table 36 above had the following characteristics:

TABLE 37

Finished Ball (from Table 36)				
Property	A	B	C	D
Flex Modulus (weighted avg.)	58 MPa	58 MPa	240 Mpa	140 MPa
Stiffness Modulus (estimate)	~300 Kgf/cm ²	~300 Kgf/cm ²	1820 Kgf/cm ²	763 Kgf/cm ²
Combined Mantle/Cover Stiffness	~700 Kgf/cm ²	~700 Kgf/cm ²	1942 Kgf/cm ²	—
Cover Specific Gravity	0.98 ± 0.01	0.98 ± 0.01	0.98 ± 0.01	0.98 ± 0.01
Size	1.685" ± 0.005	1.685" ± 0.005	1.685" ± 0.005	1.685" ± 0.05
Weight	45.4 g ± 0.4	45.4 g ± 0.04	45.4 g ± 0.4	45.4 g ± 0.04
Rieble Compression	105 ± 10	100 ± 10	95 ± 5	85 ± 5
C.O.R.	0.770 ± 0.015	0.780 ± 0.015	0.790 ± 0.015	0.790 ± 0.015
JIS C	72 ± 1	72 ± 1	93 ± 1	87 ± 1
Shore C	72 ± 1	72 ± 1	93 ± 1	87 ± 1
Shore D	46 ± 1	46 ± 1	62 ± 1	56 ± 1

An additional step of exposure to gamma radiation was performed on balls A and B of Table 37 producing golf balls having the following characteristics:

TABLE 38

Finished Balls (Post Gamma)				
Finished Ball (From Table 37)	A (Ball)	A (Core)	B (Ball)	B (Core)
Property (Post Gamma)				
Gamma Dosage (Ball)	35-70 Kgys	—	35-70 Kgys	—
Size	1.683" ± 0.003	1.47" ± 0.004	1.683" ± 0.003	1.47 ± 0.004
Thickness (Cover)	0.057" ± 0.008	—	0.057" ± 0.008	—
Weight	45.5 g ± 0.4	33.3 g ± 0.3	45.5 g ± 0.4	33.3 ± 0.3
Rieble Compression	86 ± 5	120 ± 10	81 ± 5	110 ± 10
C.O.R.	0.795 ± 0.015	0.770 ± 0.020	0.800 ± 0.015	0.780 ± 0.020
Cover Specific Gravity	0.98 ± 0.01	—	0.98 ± 0.1	—

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TABLE 38-continued

Finished Ball (From Table 37)	Finished Balls (Post Gamma)		
	A (Ball)	A (Core)	B (Core)
Core Specific Gravity	---	1.194 ± 0.05	---
JIS C	72.1	78.2	80.2
Shore C	72.1	78.2	80.2
Shore D	46.1	48.2	50.2
Dimple Pattern	422 Tri	---	422 Tri

The method of gamma radiation treatment of golf balls, including benefits and property changes attained therefrom, is taught in commonly assigned U.S. Pat. No. 5,857,925 to Sullivan et al., which is incorporated herein by reference. Benefits and/or property changes associated with gamma radiation treatment of golf balls include, but are not limited to, increased melting temperature for the ionomer cover, increased compression and C.O.R. for the core, allows softer starting materials for core, etc.

Example 9

In yet another preferred embodiment according to the present invention, golf balls having a core and a cover were formed according to the compositions provided below in Tables 39 to 41. The golf balls designated 1-4 below utilize polybutadiene rubbers which are not considered to be ultra high Mooney viscosity rubbers.

TABLE 39

Materials	Cores					
	1	2	3	4	5	7
Cariflex 1220	70	70	70	70	---	---
Taktene 220	30	30	30	30	---	---

TABLE 39-continued

Materials	Cores						
	1	2	3	4	5	6	7
BCP 820 (1220 X)	---	---	---	---	40	40	40
Neo Cis 60	---	---	---	---	30	30	30
Neo Cis 40	---	---	---	---	30	30	30
Regrind	10	20.5	20.5	17	0.2	---	---
Zinc Oxide	24.33	23	22.8	9.5	22.10	24	24
Tungsten Powder	0.17	0.17	0.17	0.17	---	0.17	0.17
Zinc Stearate	20	20	20	15	16.0	16.3	16.3
ZDA	22	22	23.2	19	24.30	20.5	20.5
Red MB	---	---	---	---	0.08	0.14	0.14
Blue MB	---	---	---	---	0.08	---	---
Yellow MB	0.14	---	---	---	---	---	---
Black MB	---	0.14	0.14	---	---	---	---
Orange MB	---	---	---	3.5	---	---	---
PolyPro 20 Mesh	---	---	---	0.15	---	---	---
231 XL or 29/40	0.9	0.9	0.9	0.9	---	---	---
Trig 42-40B	---	---	---	---	1.25	1.24	1.24

*amounts in parts per hundred resin

Golf ball cores having the following properties were produced from the core formulations of Table 39.

TABLE 40

Properties	(Core)						
	1	2	3	4	5	6	7
Size	1.543" ± 0.008	1.543" ± 0.008	1.543" ± 0.008	1.570" ± 0.008	1.540"	1.560" ± 0.005	1.56" ± 0.005
Weight	3.67" ± 0.4	36.7 g ± 0.4	36.7 g ± 0.4	35.4 g ± 0.4	36.42 g	38.0 g ± 0.004	38.0 g ± 0.004
Riche Comp.	96 ± 8	105 ± 8	92 ± 8	115 ± 10	97	113 ± 9	113 ± 9
C.O.R.	0.795 ± 0.015	0.780 ± 0.015	0.780 ± 0.015	0.773 ± 0.015	---	0.780 ± 0.010	0.780 ± 0.010
Specific Gravity	1.168 ± 0.005	1.168	1.168	1.078 ± 0.04	---	1.16	1.16
JIS C	79 ± 2	77 ± 2	80 ± 2	77 ± 1	---	73 ± 1	73 ± 2
Shore C	79 ± 2	77 ± 2	81 ± 2	79 ± 1	---	75 ± 2	75 ± 2
Shore D	49 ± 2	48 ± 2	50 ± 2	45 ± 1	---	44 ± 1	44 ± 1

The cores, as shown in Table 40, were then formed into finished golf balls by covering them with an outer cover formulation. The covers are typically ionomeric but other polymers may be utilized in the covers as set forth herein before. Ionomers typically associated with the golf balls according to the present invention include those designated as Surlyn®, manufactured by DuPont, and Iotek, manufactured by Exxon. The ionomers may be used individually or in blends. The following Table 41 includes ionomers which are exemplary of specific ionomers that may be utilized for the outer cover layer of golf balls according to the present invention.

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TABLE 41

Outer Cover Ionomers							
	Surlin 8940	Surlin 9910	Surlin 8320	Surlin 8120	Surlin 8549	Surlin 8552/6120	Surlin 8140
% Acid Type	16% MA	15% MA	~7% MA	~7% MA	15% MA	19% MA	19% MA
Ionomer Type	Copolymer	Copolymer	Terpolymer	Terpolymer	Copolymer	Copolymer	Copolymer
Cation	Na	Zn	Na	Na	Na	Na	Mg
Melt index	2.8	0.7	0.8	2	2.3	2.6	1.3
Stiffness Modulus *2	2705 Kgf/cm ²	2874 Kgf/cm ²	168 Kgf/cm ²	492 Kgf/cm ²	—	—	3499 Kgf/cm ²
	Iotek 7030	Iotek 7510	Iotek 7520	Iotek 8000	Iotek 1006	Iotek 1007	
% Acid Type	15% AA	6% AA	6% AA	15% AA	15% AA	15% AA	
Ionomer Type	Copolymer	Terpolymer	Terpolymer	Copolymer	Copolymer	Copolymer	
Cation	Zn	Zn	Zn	Na	Na	Zn	
Melt Index	2.5	0.8	2	2	1.3	0.9	
Stiffness Modulus *2	1840 Kgf/cm ²	284 Kgf/cm ²	270 MPa	3323 Kgf/cm ²	2719 Kgf/cm ²	1498 Kgf/cm ²	

AA = Acrylic Acid; MA = Methacrylic Acid

*2 Stiffness measurements done using Toyoseiki Stiffness Tester

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Finished golf balls were prepared utilizing the cores from Table 40 above, and cover materials from Table 41 above. The finished golf balls are set forth in Table 42 below.

invention be construed as including all such alternations and modifications insofar as they come within the scope of the claims and the equivalents thereof.

TABLE 42

Finished Ball	A	B	C	D	E	F	G	H
Core (From Table 40)	1	2	3	4	5	6	7	6
Cover Material(s) (Wt %)								
Surlin 8940 (Na)	10.3	—	—	—	10.3	—	22.0	—
Surlin 9910 (Zn)	26.8	—	—	—	26.8	—	54.4	—
Surlin 8320 (Na)	38.2	—	—	—	38.2	—	10	—
Surlin 8120 (Na)	15.0	—	—	—	15.0	—	1.00	—
Surlin 8549	—	—	—	—	—	—	—	—
Iotek 7030 (Zn)	9.7	9.7	9.7	9.7	9.7	9.7	9.7	9.7
Iotek 7510	—	—	—	—	—	—	—	—
Iotek 7520	—	—	—	—	—	—	—	—
Iotek 8000	—	—	—	—	—	—	—	—
Surlin 8552/6120 (Mg)	—	54.2	54.2	—	—	45.15	—	40.7
Surlin 8140 (Na)	—	36.1	36.1	—	—	—	—	—
Iotek 1006	—	—	—	36.1	—	45.15	—	46.8
Iotek 1007	—	—	—	54.2	—	—	—	—
Whitener (TiO ₂)*	3.1phr	3.1 phr	3.1 phr	3.1 phr	3.1 phr	3.1 phr	3.1 phr	3.1 phr

*Parts per hundred resin

The finished golf balls of Table 42 were found to have the following properties:

TABLE 43

Finished Golf Balls (From Table 42)						
Properties	A	B	C	D	F	G
Flex Modulus (weighted avg.)	154 MPa	472 MPa	472 MPa	201 MPa	379 MPa	276 MPa
Stiffness Modulus	<1820 Kgf/cm ²	—	—	—	—	—
Specific Gravity (Cover)	0.98 ± 0.01	0.98 ± 0.01	0.98 ± 0.01	0.99 ± 0.01	0.98 ± 0.01	0.98 ± 0.01
Size	1.685" ± 0.005	1.685" ± 0.005	1.685" ± 0.005	1.715" ± 0.005	1.685" ± 0.005	1.685" ± 0.005
Weight	45.4 g ± 0.4	45.4 g ± 0.4	45.4 g ± 0.4	45.4 g ± 0.4	45.4 g ± 0.4	45.4 g ± 0.4
Riehle Comp.	90.5	75.5	70.5	90 ± 5	95 ± 5	97 ± 3
C.O.R.	0.790 ± 0.015	0.810 ± 0.010	0.810 ± 0.010	0.805 ± 0.012	0.806 ± 0.009	0.803 ± 0.005
JIS C	85 ± 1	99 ± 1	99 ± 1	95 ± 3	95 ± 1	91 ± 1
Shore C	87 ± 1	99 ± 1	99 ± 1	97 ± 1	97 ± 1	93 ± 1
Shore D	59 ± 1	73 ± 1	73 ± 1	68 ± 1	69 ± 1	65 ± 1

The invention has been described with reference to the preferred embodiments. Obviously, modifications and alterations will occur to others upon reading and understanding the preceding detailed description. It is intended that the

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Having thus described the preferred embodiment, the invention is now claimed to be:

1. A golf ball comprising:

a core including (i) a first polybutadiene rubber obtained utilizing a nickel and/or cobalt catalyst and having a Mooney viscosity in the range of from about 65 to about 85 and a polydispersity in the range of about 1.9 to about 3.9 and (ii) a blend of a second and third or more polybutadiene rubbers wherein each is obtained by utilizing a lanthanide series catalyst and having a Mooney viscosity of from about 30 to about 65; and a cover disposed about said core.

2. The golf ball of claim 1 wherein said first polybutadiene rubber includes at least 90% cis-1,4 polybutadiene.

3. The golf ball of claim 2 wherein said first polybutadiene rubber includes at least 95% cis-1,4 polybutadiene.

4. The golf ball of claim 1 wherein said first polybutadiene rubber has a polydispersity in the range of from about 2.4 to about 3.1.

5. The golf ball of claim 1 wherein said blend of polybutadiene rubbers comprises a first polybutadiene having a Mooney viscosity of about 40 and a second polybutadiene having a Mooney viscosity of about 60.

6. The golf ball of claim 1 wherein said first polybutadiene rubber is present in an amount of about 40% by weight of the rubber composition of the core.

7. The golf ball of claim 1 wherein said blend of polybutadiene rubbers is present in an amount of about 60% by weight of the rubber composition of the core.

8. The golf ball of claim 7 wherein said blend of polybutadiene rubbers is comprised of about 30% by weight of a first polybutadiene having a Mooney viscosity of about 40 and about 30% by weight of a second polybutadiene having a Mooney viscosity of about 60.

9. A golf ball comprising:

a core including a blend comprising of (i) about 45 parts by weight or less of a first polybutadiene rubber, wherein said first polybutadiene rubber is obtained utilizing a nickel and/or cobalt catalyst and having a

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Mooney viscosity in the range of from about 65 to about 85 and, (ii) about 55 parts by weight or more of at least a second or third polybutadiene rubber, wherein said second or third polybutadiene rubber is obtained utilizing a lanthanide series catalyst and having a Mooney viscosity of from about 30 to about 65; and a cover disposed about said core.

10. The golf ball of claim 9 wherein said first polybutadiene rubber includes at least 90% cis-1,4 polybutadiene.

11. The golf ball of claim 10 wherein said first polybutadiene rubber includes at least 95% cis-1,4 polybutadiene.

12. The golf ball of claim 9 wherein said first polybutadiene rubber has a polydispersity in the range of from about 1.9 to about 3.9.

13. The golf ball of claim 12 wherein said first polybutadiene rubber has a polydispersity in the range of from about 2.4 to about 3.1.

14. A golf ball comprising:

a core including a blend comprising of (i) about 40 parts by weight or less of a first polybutadiene rubber obtained utilizing a nickel and/or cobalt catalyst and having a Mooney viscosity in the range of from about 70 to about 83 and, (ii) about 60 parts by weight or more of a second polybutadiene rubber obtained by utilizing lanthanide series catalyst and having a Mooney viscosity of from about 30 to about 70; and a cover disposed about said core.

15. The golf ball of claim 14 wherein said first polybutadiene rubber includes at least 90% cis-1,4 polybutadiene.

16. The golf ball of claim 15 wherein said first polybutadiene rubber includes at 95% cis-1,4 polybutadiene.

17. The golf ball of claim 14 wherein said first polybutadiene rubber has a polydispersity in the range of from about 1.9 to about 3.9.

18. The golf ball of claim 15 wherein said first polybutadiene rubber has a polydispersity in the range of from about 2.4 to about 3.1.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,612,940 B1
DATED : September 2, 2003
INVENTOR(S) : R. Dennis Nesbitt et al.

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title page,

Item [63], **Related U.S. Application Data,**

"This application is a Continuation of application No. 09/490,181, filed on January 22, 2002, now Pat. No. 6,422,953, which is a" should be inserted before "Continuation-in-part of application No. 09/371,994, filed on Aug. 11, 1999". Also, "Provisional application No. 60/116,846, filed on Jan. 22, 1999, provisional application No. 60/116,899, filed on Jan. 22, 1999, provisional application No. 60/116,900, filed on Jan. 22, 1999, and provisional application No. 60/117,328, filed on Jan. 22, 1999" should read- - Provisional application No. 60/116,846, filed on Jan. 22, 1999, provisional application No. 60/116,899, filed on Jan. 22, 1999, provisional application No. 60/116,900, filed on Jan. 22, 1999, provisional application No. 60/117,328, filed on Jan. 22, 1999, provisional application No. 60/116,901, filed Jan. 22, 1999, and provisional application No. 60/116, 870, filed on Jan. 22, 1999- -.

Signed and Sealed this

Twenty-third Day of March, 2004



JON W. DUDAS
Acting Director of the United States Patent and Trademark Office

EXHIBIT 3

The charts below show how the limitations of the asserted claims are disclosed in the Nesbitt '940 patent.

Summary Chart for Claim 1:

Claim 1 of the '961 Patent	The Nesbitt '940 Patent
A multi-piece solid golf ball comprising, a solid core, an inner cover layer and an outer cover layer, wherein the solid core is molded from a rubber composition	Nesbitt '940 also relates to a multi-piece solid golf ball, with a solid core, an inner cover layer and an outer cover layer. (Nesbitt '940, at Abstract; col. 16, lines 49-57; col. 44, lines 60-65; Tables 6, 30-37)
comprising 100 parts by weight of a base rubber composed of	Nesbitt '940 describes a core formulation made up of 30 parts Neo Cis 60, 30 parts Neo Cis 40 and 40 parts Cariflex 1220x, which accounts for 100 parts by weight of the base rubber. (Nesbitt '940 at Tables 6 and 30).
(a) 20 to 100 wt % of a polybutadiene having a cis-1, 4 content of at least 60% and 1,2 vinyl content of at most 2%, having a viscosity η at 25° C. as a 5 wt % solution in toluene of up to 600 mPa.s, being synthesized using a rare-earth catalyst and satisfying the relationship: $10B + 5 \leq A \leq 10B + 60$, wherein A is the Mooney viscosity (ML1+4(100° C.)) of the polybutadiene and B is the ratio Mw/Mn between the weight-average molecular weight Mw and the number-average molecular weight Mn of the polybutadiene,	Nesbitt '940 describes a core formulation made up of 30% Neocis 60, which is a polybutadiene rubber synthesized from a rare earth catalyst that inherently possesses the claimed limitations relating to cis-1,4 content, 1,2 vinyl content, solution viscosity, Mooney viscosity and polydispersity of the '961 patent. (Nesbitt '940 at Tables 6 and 30).
in combination with (b) 0 to 80 wt % of a diene rubber other than component (a)	Nesbitt '940 describes a core formulation made up of 30% Neo Cis 40 and 40% Cariflex 1220x, which are both diene rubbers and account for 70% of the total base rubber. (Nesbitt '940 at Tables 6 and 30).
(c) 10 to 60 parts by weight of an unsaturated carboxylic acid or a metal salt thereof or both	Nesbitt '940 describes a core formulation made up of 18.2 and 20.5 parts by weight of zinc diacrylate (ZDA), which is a metal salt of an unsaturated carboxylic acid. (Nesbitt '940 at Tables 6 and 30).

(d) 0.1 to 5 parts by weight of an organosulfur compound	Nesbitt '940 incorporates by reference, the organic sulfur compounds disclosed in U.S. Patent No. 4,852,884 to Sullivan in an amount of 0.1 to 0.5 parts by weight. (Nesbitt '940, col. 13, lines 25-32).
(e) 5 to 80 parts by weight of an inorganic filler	Nesbitt '940 describes a core formulation made up of 24 and 31.4 parts by weight of zinc oxide, which is an inorganic filler. (Nesbitt '940 at Tables 6 and 30).
(f) 0.1 to 5 parts by weight of an organic peroxide;	Nesbitt '940 describes a core formulation made up of 1.24 and 1.25 parts by weight of Triganox 42-40B, which is an organic peroxide. (Nesbitt '940 at Tables 6 and 30).
the inner cover layer has a Shore D hardness of 50 to 80; the outer cover layer has a Shore D hardness of 35 to 60; and the outer cover layer has a lower Shore D hardness than the inner cover layer.	Nesbitt '940 describes an inner cover with a Shore D hardness of 70 and an outer cover with a Shore D hardness of 46. (Nesbitt '940 at Tables 34 and 37).

Summary Chart for Claim 2:

Claim 2 of the '961 Patent	The Nesbitt '940 Patent
The golf ball of claim 1,	As described above, Nesbitt '940 teaches each and every limitation of claim 1.
wherein the diene rubber (b) includes 30 to 100 wt % of a second polybutadiene	<p>Nesbitt '940 discloses a core formulation made up of three rubbers: (a) 30 parts of Neocis 60; (b) 30 parts of Neocis 40; and (c) 40 parts of Cariflex 1220x.</p> <p>From claim 1, Neocis 40 and Cariflex 1220x are read as diene rubber (b).</p> <p>Neocis 40, which is a second polybutadiene rubber, accounts for 30 of the 70 parts of diene rubber, which is 43% of the diene rubber.</p> <p>(Nesbitt '940 at Tables 6 and 30).</p>
which has a cis-1, 4 content of at least 60% and a 1,2 vinyl content of at most 5%, has a Mooney viscosity (ML1+4(100°C.)) of note more than 55, and satisfies the	Neocis 40 is a polybutadiene rubber that inherently possesses the claimed limitations relating to cis-1,4 content, 1,2 vinyl content, solution viscosity and

relationship: $\eta \leq 20A - 550$, wherein A is the Mooney viscosity (ML1+4(100°C.)) of the second polybutadiene and η is the viscosity of the second polybutadiene, in mPa.s, at 25° C. as a 5 wt % solution in toluene.	Mooney viscosity. (Nesbitt '940 at Tables 6 and 30).
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EXHIBIT 4

**THIS EXHIBIT HAS BEEN
REDACTED IN ITS ENTIRETY**

EXHIBIT 5

**THIS EXHIBIT HAS BEEN
REDACTED IN ITS ENTIRETY**